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The Rev. John Carne, Penzance; J. Whitaker Hulke, Esg., F.R.S., F.C.S., 10 Old Burlington Street, W.; and Lewis Thomas Lewis, Esq., Gadlys, Aberdare, were elected Fellows.

The following communications were read :---

1. On the DISPOSITION of IRON in VARIEGATED STRATA. By George Maw, Esq., F.L.S., F.G.S., &c.

(PLATES XI.-XV.)

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- 6. The variegation of the Keuper marts.
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OF those secondary changes which have modified the original chemical and physical constitution of rocks none seem to have more VOL. XXIV .--- PART I. 2 c

largely affected their aspect than the recombinations and rearrangement of iron.

In continuation of this subject, treated of in a short paper read before this Society last year *, the following communication records some further observations on those forms of ferruginous variation which appear to have been due to secondary causes, subsequent to original mechanical deposition.

1. *Literature*.—It may be convenient in the first place to give a short résumé of the previous geological and chemical papers that directly refer to, or bear on the subject.

Sir Henry James, in a short paper dated May the 15th 1843, published in the 'London, Edinburgh, and Dublin Philosophical Magazine' for July 1843, notices that the disposition of the bluishgreen discoloration of the Old and New Red Sandstones is independent of stratigraphical arrangement, and suggests that, as the light lines and blotches are generally adjacent to joints, the cause of the discharge of colour is due to infiltration. The author, in a note to this paper, also refers to an observation by Mr. Mallet, that "if through a fissure in a rock containing peroxide of iron a stream of water should pass containing an earthy sulphate and organic matter, the sulphate will be decomposed, and sulphuretted hydrogen evolved, which might reduce the peroxide of iron to a lower oxide." With reference to this suggestion, I will here only observe that the presence of sulphate of lime in the Keuper marls of Cheshire and Derbyshire seems to have no relation to their variegation, as the bands and crystals of gypsum occur in contact with both the red and the grey portions, and, furthermore, the grey blotches in the marl often occur independently of the presence of joints.

Sir Henry de la Beche, in the first volume of the 'Memoirs of the Geological Survey,' published in 1846, p. 254, refers to the alternation at Aust Cliff, Gloucestershire, of red marls of the Keuper with blue or greenish bands, and gives analyses of each, indicating a nearly similar composition, excepting that the iron in the blue marls was said to exist wholly in a state of protoxide, and in the red as a mixture of protoxide and sesquioxide, the amount of iron in each being nearly identical; and he attributes the difference of colour to the reduction of sesquioxide to protoxide by the agency of decaying organic matter in the lighter parts of the marl. At pp. 52, 53, 57, & 267, reference is also made to the particoloured strata of the Old Red Sandstone, in the grey beds of which carbonaceous matter and protoxide of iron are said to occur, whilst in the red beds the iron was found to be wholly in a state of sesquioxide.

The next paper bearing on the subject is one by Dr. J. W. Dawson, in the Quarterly Journal of the Geological Society, vol. v. p. 25, read May 31st, 1848, relating to the red beds of Nova Scotia. It discusses the question whether the sesquioxide of iron colouring them is in its primordial condition, or the result of a secondary change from the decomposition of iron pyrites; which latter view the author supports, and attributes the blotchy discoloration to the

* Quart. Journ. Geol. Soc. vol. xxiii. p. 114.

reconversion of the sesquioxide into bisulphide by the action of sulphuretted hydrogen produced in the decay of organic matter, and supposes that a discharge of colour may also have been due to the acids produced in the putrefaction and decay of moist vegetable matter.

Dr. Sterry Hunt, in a paper on "Chemical Geology," read before this Society, June 5th 1859, and published in vol. xv. of the Quarterly Journal, et also supports the view of Dr. Dawson, that the elimination of iron from some sedimentary strata is due to the reduction of the sesquioxide to a soluble protoxide by the action of organic matter.

Mr. H. C. Sorby, in a paper on the origin of slaty cleavage, in the 'Edinburgh New Philosophical Journal' for July 1853 (p. 3), incidentally refers to the bleaching of slates, and attributes the formation of the pale blotches to "concretions of a peculiar kind formed round bodies lying in the plane of bedding."

Mr. H. C. Sorby, in a paper in the 'Proceedings of the Geological and Polytechnic Society of the West Riding of Yorkshire' for 1856-57, "On the Origin of the Cleveland Hill Ironstone," describes the replacement of carbonate of lime by carbonate of iron in shelly limestone from the Inferior Oolite—a process which will have to be referred to as a probable agent in the production of a peculiar form of variegation in the Northamptonshire Oolites.

Mr. Pengelly, in a paper on the "Red Sandstones, Conglomerates, and Marls of Devonshire," read before the Plymouth Institution and Devon and Cornwall Natural History Society, March 19th 1863, and published in the 'Transactions' of that body for 1862–63, pp. 15–38, dissents from the conclusions of Dr. Dawson, that the colour of red beds is the result of a secondary process, and enters minutely into the circumstances of the variegation of the red beds of Devonshire. To this valuable memoir I shall have occasion further to refer in the body of the paper. Although the author expresses no definite conclusions, I believe the facts pointed out for the first time by Mr. Pengelly are suggestive of the true explanation of many of the phenomena of variegation, and, I may add, agree with the views I suggested in the paper read last year before the Society, although I was not at the time aware of several of the facts Mr. Pengelly had recorded.

In a paper on the "Chemistry of some Carboniferous and Old Red Sandstones," read by Mr. J. W. Young before the Geological Society of Glasgow in March 1867, the light blotching of Red Sandstones is attributed to the presence of some organism in the sand, the decomposition of which has reduced the sesquioxide to protoxide of iron, which would be subsequently removed as carbonate by water containing carbonic acid percolating the mass; and reference is made in this paper to an observation by Mr. James Bennie, "that sand in contact with decaying roots or twigs is often found to be partially bleached."

The paper by Mr. Edward Davies, of Liverpool, on the "Action of heat or ferric hydrate in presence of water," at p. 69 of vol. iv. (new series), for 1866, of the 'Journal of the Chemical Society of London,' records some important experiments bearing on the subject of the colour of red beds.

Professor Brush, of Yale College, U. S., in a paper on the "Native Hydrates of Iron," at p. 219 of the vol. for 1867 (new series, no. xliii.) of the 'American Journal of Science,' describes the characters of several definite hydrous sesquioxides of iron, and also refers to the investigations of Mr. Davies as doing away with the necessity of the supposition of great heat to account for the presence of anhydrous hæmatite.

Dr. J. Low, in a paper on the "Carstone of West Norfolk," read before the British Association at Norwich, this year, attempts to explain the formation of ferruginous nodules in the white sands of the Lower Greensand by the infiltration of ferruginous matter and its segregation around organic substances.

On the subject of the bleaching of ferruginous rocks by organic matter, I would also refer to a paper by Kindler, published in 'Poggendorff's Annalen' (vol. xxxvii. p. 203), and noticed in 'Bischof's Chemical and Physical Geology' (vol. i. p. 166, English edition), and also to Bischof's own experiments on the reduction of sesquioxide of iron to protoxide by organic matter ('Chemical and Physical Geology,' English edition, vol. iii. p. 1), as bearing on the theory advanced by Dr. Dawson, but which seems to be only of limited application in accounting for the variegation and discoloration of red beds.

2. The States of Combination of Iron in the principal Stratified Rocks.—To more readily describe the various forms of mottling and variegation which are the subject of the following analysis, it will be necessary to refer to the states of combination of the iron pervading the principal stratified rocks as a colouring-matter.

Very prominent in connexion with the subject of variegation are the red beds, including the Trias and Devonian, and also portions of the Carboniferous, Permian, Tertiary, and other formations, which are coloured with from 4 to 15 per cent. of the anhydrous sesquioxide, and contain, also, small amounts of hydrous sesquioxide, carbonate of protoxide, and silicates of iron.

The following analysis, by Mr. David Forbes, of red elay occurring as a stratum 7 or 8 feet thick at about the middle of the Shropshire Coal-measures, may be taken as representing the general composition of the unaltered portions of many red beds that have been subject to partial bleaching.

Analysis No. 74. Red "Tile Clay," Shropshire Coal-measures, Calcotts, near Broseley. (The coarse particles had been previously removed by passing the clay through a fine lawn sieve.)

Silica combined, 29.71 Silica free, 34.35	64.06
Silica free, 34.35	0100
Titanic acid	0.62
Alumina	20.60
Sesquioxide of iron	6.84
Protoxide of iron	0.32
Protoxide of manganese	0.09

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Lime	0.12
Magnesia	0.04
Potash	0.91
Soda	0.44
Water with traces of organic matter	5.85
0	

99.89

The following analyses, however, indicate that the depth of colour of similar strata charged with the red anhydrous sesquioxide is less directly related to the *amount* of colouring-matter present than to its state of subdivision; for instance, the red clays of the Argile plastique of the Paris Basin, and of the variegated Neocomian beds near Beauvais, contain nearly 20 per cent. of red sesquioxide, whilst many sandstones of similar colour contain less than from one-fourth to one-eighth of the amount. In the one case it is in a state of fine subdivision, evenly disseminated, throughout, and intimately associated with the mass, whilst in the red sandstones it frequently occurs merely as a surface-coating to the individual grains, as, for example, in the red Millstone-grit of Cumberland, and part of the Keuper of Shropshire.

In the Old Red Sandstone of Forfarshire the colour seems to be evenly disseminated through the grains, and to have been derived from the breaking-up of an older red rock. In tracing the sources of materials from which red beds have been derived, the mechanical condition of the colouring oxide is a point of considerable interest, as indicating whether they were formed from original red beds or by the association of ferruginous matter with the other detritus at the time of deposition.

Many grey and bluish-grey beds contain a large proportion of sesquioxide of iron. Its precise condition seems to be scarcely understood, and to be worth fuller investigation. In some cases its normal red or yellow colour is evidently obscured by the presence of carbonaceous matter; but in many grey beds which contain, by analysis, a large proportion of sesquioxide of iron, the amount of carbon is not nearly enough to account for the obliteration of the normal red or yellow colour. The colours of the anhydrous and hydrous sesquioxide are given in figs. 1 & 2, Pl. XI. Burnt red earthenware, red bricks, and Venetian-red may be cited as familiar examples of the colour of the anhydrous form. The hydrous sesquioxide imparts a tint ranging from dull brown to bright yellow; and its presence in association with the anhydrous form tends to reduce the brilliancy of the colour of red beds. There are also several lower hydrates of sesquioxide intermediate in colour between the fully hydrous and the anhydrous form; but it is not practicable to distinguish them by analyses in the presence of aluminous and other hydrates.

When occurring separately in juxtaposition, as in the Folkestone beds of the Lower Greensand and in the Lower Bagshot beds, the rich blood-red of the anhydrous sesquioxide and the golden yellow of the fully hydrous sesquioxide form a marked contrast; but when they are concentrated to the extent of 15 or 20 per cent. in the matrix, they generally both assume a brown colour, and are not so easily distinguished.

Of the colour of the carbonate of protoxide (fig. 3, Plate XI.) the cold grey of Purbeck marble and some limestones may be mentioned as examples. Between this cold-grey and the yellow and brown varieties every gradation of colour occurs, in proportion to the extent of admixture with the hydrous sesquioxide, which is readily formed as a secondary product by the peroxidation of the carbonate.

The hydrous sesquioxide, which occurs so universally as the colouring-matter of yellow sandstones, appears often to have been a secondary product, formed by the hydration of the anhydrous sesquioxide; and the carbonate of protoxide of iron taken up in a state of solution by an access of carbonic acid, becomes immediately on redeposition converted into the hydrous sesquioxide, a familiar example of which occurs in the formation of ochreous tufa on the deposition of the carbonates of lime and iron from carbonated springs.

In contrast with the unstable character of the carbonate of iron deposited from a carbonated solution, may be noticed the permanent condition of the mineral carbonate occurring in the form of segregated nodules in, and evenly distributed through, strata charged with carbonaceous matter—a fact to be referred to in considering the probability of the bleached patches in red beds being due to the presence of organic matter.

Of the strata containing protocarbonate of iron may be enumerated the grey beds of the Coal-measures, the Oolites, and the Tertiaries, of which the following are some analyses.

Analysis No. 30, of Grey Clay from Bovey Tracey Lignite deposit.

Protoxide of iron 0.49 per cent.

Analysis No. 31, of Ganie Clay (Fire-clay), Shropshire Coal-measures. Protoxide of iron 1.48 per cent.

Analysis No. 32, of Pennystone Clod, Shropshire Coal-measures, Benthall, near Broseley.

Protoxide of iron 3.75 per cent.

These determinations do not include the carbonate of iron occurring as segregated nodules.

Analysis No. 36, by Dr. Voelcker, of Grey Clay, Coal-measures, Wyre Forest, Worcestershire.

Analysis No. 37, by Dr. Voelcker, of London Clay, Bawdsey Cliff, Suffolk.

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Analysis No. 64, by Dr. Voelcker, Kimmeridge Clay, Chapman's Pool, near Kimmeridge, Dorsetshire.

Protoxide of iron Sesquioxide of iron	1.04
Bisulphide of iron	$0.86 \begin{cases} \text{Sulphur } 0.46 \\ \text{Iron } \dots 0.40 \end{cases}$
Sulphate of lime Carbonate of lime	0.35 per cent.

Analysis No. 65, by Dr. Voelcker, Kimmeridge Clay, near Calne.

Protoxide of iron	2.08 per cent.
Sesquioxide of iron	4.32 ,,
Bisulphide of iron	$1.42 \begin{cases} \text{Sulphur } 0.76 \\ \text{Iron } \dots 0.66 \end{cases}$
Sulphate of lime	5.34 per cent.
Carbonate of lime	4.28 "

Analysis No. 66, by Dr. Voelcker, Oxford Clay, Brick-works, Canal Bank, Chippenham.

Protoxide of iron	1.12 per cent.
Sesquioxide of iron	3.25 "
Bisulphide of iron	$1.10 \begin{cases} \text{Sulphur } 0.59 \\ \text{Iron } \dots & 0.51 \end{cases}$
Sulphate of lime	1.37 per cent.
Carbonate of lime	none.

The carbonate of protoxide has but a weak colouring-power; and the grey colour of the strata in whch it occurs is generally due to the presence of carbonaceous matter, which also obscures the colour of any accompanying sesquioxide of iron.

Bisulphide of iron occurring in mechanical admixture is common to beds of all ages and colours, and has but little colouring-power.

Iron pervading the older slate rocks occurs in almost every state of combination, and in all varieties of proportion, in some of the Cambrian slates almost exclusively as sesquioxide, and in others as protoxide.

Iron also occurs to some extent, with a weak colouring-power, as the basic sulphate of sesquioxide in beds in the lower part of the Ashdown Sands. Its production from the decomposition of iron pyrites will have to be referred to in accounting for some forms of variegation.

3. On the Primary Condition of Iron in Red Beds.—As a necessary introduction to the subject of the blotching of ferruginous strata, reference must be made to the question discussed by Dr. Dawson, on the origin of the colour of red beds, and the primary condition under which the iron was deposited. Dr. Dawson (Quarterly Journal of the Geological Society, vol. v. p. 25), in describing the red beds of Nova Scotia, suggested that the sesquioxide of iron pervading them was derived from the oxidation of bisulphide of iron under the influence of heat and moisture; he stated that bisulphide of iron is largely developed in the older rocks of Nova Scotia, and that there is no apparent earlier source for the iron in a state of sesquioxide. For the details of Dr. Dawson's views I would refer to his paper, and will here only state the grounds upon which they seem open to question.

In the first place, the condition in which the iron occurs in brightred clays and sandstones is principally that of the anhydrous, or slightly hydrous sesquioxide, whilst the sesquioxide ultimately derivable from the decomposition of pyrites is the yellow hydrous form. This, however, is not a fatal objection, as the experiments of Mr. Edward Davies, F.C.S., of Liverpool, recorded at p. 69 of the fourth volume of the new series of the Chemical Society's Journal, prove the possibility of the hydrous ferric oxide being reduced to a brick-red subhydrate, containing only from 4 to 5 per cent. of water, by prolonged heat in the presence of water, at temperatures considerably below the boiling-point.

The occurrence in common of bisulphide of iron both in red beds and in those containing carbonate of iron supplies an argument against the derivation of the red sesquioxide from its decomposition; indeed the decomposition of pyrites seems occasionally to have caused the obliteration of a preexisting red colour, instead of having been the agent in its production; but this point will be considered further on, in connexion with the causes of variegation.

Dr. Dawson further suggests that sulphate of lime in red beds may be an incidental product of the oxidation of pyrites in contact with calcareous matter; but the association of red marks and gypsum is by no means general. On the one hand, many red marks containing calcareous matter are entirely devoid, or contain but a mere trace, of sulphate of lime *; and on the other, gypsum and selenite as frequently occur in grey beds containing carbonate of iron, as, for instance, in the Lower Purbecks, Oxford Clay, Kimmeridge Clay, the French Tertiaries, and the grey marks of the Muschelkalk; and the occurrence of sulphuric acid seems to have no regular relation to the presence of either protoxide or sesquioxide of iron in strata.

The physical evidence in favour of the primordial occurrence of the anhydrous sesquioxide seems also as strong as the chemical. In the first place, there seems no primá facie reason for the greater probability of the detrital accumulation of the bisulphide than of the red sesquioxide; if the bisulphide were specially characteristic of the earlier rocks, and the red sesquioxide of the more recent deposits, the probability of the derivation of the latter suggested by Dr. Dawson might be implied; but, as a matter of fact, disseminated bisulphide of iron is much more abundant in the Oolites, London Clay, &c. than in the earlier rocks of Cambrian and Silurian age; and, furthermore, the earliest red beds (for example the Old Red Sandstone), containing red pebbles not merely surface-coated, but red throughout their mass, prove the detrital derivation of their red colour from an earlier red rock. The red colour of the pebbles is clearly not the result of a change of colour affecting the entire mass of the old red beds; for they are associated in the red matrix

* See Analysis of Keuper marls, given at p. 370, Carboniferous marls, p. 365, and Marnes Irisées, p. 384.

with fragments of other rocks of various colours, which have not been so changed, and also with derivative fragments of dark-red marl containing more sexquioxide of iron than the general matrix.

4. On the Bleaching of Red Beds due to Abstraction of the Colouring Oxide.—Whatever may have been the primordial condition of the sesquioxide of iron pervading red beds, the occurrence of pale blotching seems to have almost invariably supervened on a uniformly red colour; in short, the pale portions have been produced on a red matrix, and not the red colour partially introduced on a lighter ground. This is a point at once rendered obvious by the relative disposition of the light and dark colours.

The several forms presented by the blotching of red beds have been fully described with reference to the red beds of Devon in the Memoir by Mr. Pengelly already noticed; and the accompanying illustrations (figs. 4–11, Plate XI.; 12–16, Plate XII.; 27, Plate XIV.; and figs. 41, 42, 44, 45, 49, *infrà*) represent the principal characteristics presented by the phenomena in various formations. Of all the forms that variegation takes, the occurrence of isolated blotches environed on all sides by the primordial colour seems to be most obviously independent of mechanical arrangement. In the red beds of the Bunter, Keuper, Permian, and Carboniferous, such blotches are of common occurrence, and are more often than otherwise independent of any apparent predisposing cause.

In some instances, especially in the Keuper beds, the blotches seem to have a tendency to range with the stratification; and the lines of unconnected light patches (fig. 13, Plate XII.) merge by insensible gradations into regular stratified beds of alternating colour. In other cases, as in the Permian and Grès bigarré (figs. 8 & 9, Plate XI., and fig. 12, Plate XII.), the blotching is altogether independent of the lie of the beds; and fields of light colour, obviously of secondary origin, vertically intersect alternating strata of different physical character and composition; and in contrast with this apparently adventitious disposition must be noticed the occurrence of light bands and blotches, the localization of which is evidently connected with a predisposing cause, such as the existence of vertical and horizontal joints, and of mechanical nuclei, as pebbles of various rocks, fragments of fossils, &c.

Perhaps the most perplexing point in connexion with the phenomena is, on the one hand, the apparently adventitious occurrence of the discoloured areas, and, on the other, their occasional connexion with predisposing causes—and yet, at the same time, the evident identity of the two extremes, which are connected by every variety of intermediate grade: for instance, variegation apparently determined by a line of joint will branch out and spread itself irregularly into an unjointed mass, and this again leads up to a group of isolated blotches; again, blotches formed concentrically round a mechanical nucleus, may be closely associated with blotches having no such centre, and blotches both with and without a nucleus of segregation may occur on the same piece of stone.

Another point to be noticed is the entire independence of the

range of these discoloured areas in relation to the mechanical composition of the stratum, which is well shown in fig. 14, Plate XII., representing a portion of the Old Red Conglomerate of Forfarshire, composed for the most part of red pebbles held together by a comminuted sandstone of the same material. In this example the blotches of secondary discoloration range in common through the impervious pebbles and the red matrix. In some instances the chemical nuclei of the light blotches occur in the sandstone ground, whilst the range of bleaching extends into the pebbles that happen to come within its radius; and in others the segregated nucleus occurs in the very body of the pebble, whilst the circumscribing area of discoloration spreads itself in common partly through the pebble and partly through the surrounding sandstone.

A more singular case than this occurs in the Carboniferous Limestone at Trevor, near Llangollen, where an interstratified layer of red gravel (fig. 7, Plate XI.), probably derived from the Old Red beds, is permeated by bands of greenish discoloration, which run through the loose mass, affecting the one half of individual pebbles that intersect its line of boundary, leaving the other half unchanged. This partial change of colour cannot be the effect of mere infiltration, because the pebbles lie loosely without the slightest cohesion, so that any water passing through one part of the bed must have pervaded the whole mass.

The more common forms of variegation of red beds are so familiar to geological observers that any further general description is unnecessary, and it now remains to consider the chemical composition of the several coloured areas.

The following analyses have been made with special reference (1) to the amount of the colouring oxide and of the metallic base, (2) to its state of combination in the several coloured areas, and (3) to general composition in relation to variation of colour.

The first example (Analyses, Nos. 6, 7, 8) is a nucleated form of variegation of Permian Sandstone near Coalport, Shropshire (fig. 9, Plate XI.), viz. a red ground mottled with light blotches concentrically surrounding much darker nuclei.

No.

6.	The	red g	round o	contain	ed	Protoxide of iron	0.538 Metallic iron
		39	. ,,		99 ·	Sesquioxide of iron	$1.520 \int 1.470$ per cent.
7.	The	dark	central	nucleu	ıs	Protoxide of iron	0.646 Metallic iron
		,,	,,		3 3	Sesquioxide of iron	12.260 \$ 9.000 per cent.
8.	Ligh	t zone	, surrou	inding	nucleus	Protoxide of iron	0.010 Metallic iron
	0		,			Sesquioxide of iron	0.700 \$ 0.491 per cent.

A somewhat similar disposition of colour occurs in the Permian Sandstone penetrated in sinking the new coal-pits at Kemberton, near Madeley, Shropshire (fig. 8, Plate XI.), in which not only the spherical nucleated blotches occur, but also discoloured bands with a central dark line of sesquioxide of iron *intersecting obliquely the beds of stratification*—a fact which suggests that the variegation in this case could not have been induced by anything interbedded with the deposition of the sandstone.

In some examples of this class of variegation the dark nuclei occur in such close contiguity that the whole of the original red ground seems to have been exhausted, leaving a uniformly light field containing the dark spots of segregation irregularly disposed. In some portions of the Millstone-grit the individual nuclei of the rearranged sesquioxide of iron are so small that they give portions of the sandstone a freckled appearance, lighter than the general red ground, with which they alternate in irregular blotches. This is seen in the Carboniferous sandstone (Millstone-grit?) that overlies the Mountain-limestone at Lamanby and Blencow, near Penrith, of which the Penrith station is built. Some of the larger dark blotches are also nuclei of segregation; but most of them are mechanically rounded lumps of soft hæmatite, occurring both in the red and the discoloured portions. Such a combination of mechanical and secondary causes occasionally produced some singularly complex arrangements of colour, which at a first glance are difficult to understand.

The points to be particularly noticed with reference to the Coalport example are, 1st, that the bleached zone appears due to the withdrawal of the colouring sesquioxide from the red ground into the central nucleus, the one containing less and the other more than the normal colour, and, 2ndly, that there is no evidence of change in the state of combination of the iron, except that the segregated sesquioxide becomes hydrous. In all three shades of colour the iron principally occurs as sesquioxide; and the slight differences of the proportions of protoxide and sesquioxide are so irregular that they appear unconnected with the variegation.

Some remarkable forms of this tricoloured variegation occur in the Grès des Vosges, or Upper Permian, of the East of France. Fig. 6 (Plate XI.) represents an example of fissile flagstones from the south of Raon l'Etape, Vosges, in which bleached layers occur ranging with the stratification, accompanied by the rearrangement of the sesquioxide of iron as dark nuclei in the bleached bands; and in some stones of the Grès bigarré or Lower Trias in the basement of the Palace of Industry, Paris (fig. 12, Plate XII.), the red sesquioxide has become converted into the yellow hydrous sesquioxide, accompanied by its segregation into nuclei which are ranged in lines near the boundary of the area of discoloration.

The Lower Bagshot beds near Wareham (fig. 23, Plate XIII.) present some complicated arrangements of colour due to secondary causes, of a somewhat similar character. The primordial bright red colour of these variegated beds was evidently due to anhydrous sesquioxide of iron; this has assumed the hydrous condition in irregular yellow blotches, and in places it has become segregated into a multitude of small nodular concretions, surrounded by light-grey bleached zones from which the iron has been abstracted; by this process a singularly beautiful mottling of four distinct colours has been produced out of an original uniformly red bed.

A precisely similar form of variegation exists in the Neocomian beds in the neighbourhood of Beauvais, France, where fields of bright red and yellow interlace, here and there accompanied by nodular concretions of segregated sesquioxide.

Another phase of variegation, noticed in Mr. Pengelly's memoir on the red beds of Devon, consists of discoloured zones concentrically surrounding a pebble, fragment of fossil, or other mechanical nucleus, and evidently localized by the occurrence of such nucleus. The Old Red beds of Scotland (fig. 14, Plate XII.) and the red conglomerates of Devon (fig. 5, Plate XI.) contain frequent examples of such loss of colour; and fig. 4 (Plate XI.) represents zones of discoloration surrounding mechanical fragments of shale in the Grès bigarré, near Raon l'Etape, Vosges.

Among the various mechanical nuclei that seem to have determined the position of these spheres of discoloration, fragments of Devonian limestone in the red beds of Devon are of frequent occurrence. In a discussion on a previous paper relating to this subject, read during the late session of the Society (1867), it was suggested by Mr. Godwin-Austen that the fragments of carbonate of lime might have arrested the peroxidation of the iron, or reduced the sesquioxide to a state of protoxide in immediate contact with them, and thus have produced the zone of discoloration without removing the metallic base.

I have obtained through the kindness of Mr. Pengelly an example of such discoloration from Torbay (fig. 5, Plate XI.), and procured a determination of the iron and lime in the red ground and the area of discoloration.

Analysis No. 9, of the discoloured zone, indicated 0.81 per cent. of iron almost wholly in a state of sesquioxide, with a small amount, viz. 0.15 per cent., of protoxide.

Analysis No. 10, of the red ground, gave 2.88 per cent. of iron, nearly all of which occurred as sesquioxide, and about 0.10 per cent. as protoxide.

Both the red and the discoloured portions contained the same amount of lime, viz. 7.84 per cent. No connexion can therefore be traced between the chemical action of the limestone and the bleaching of the adjacent zone; and we have here again merely the departure of the greater part (in round numbers three-fourths) of the colouring oxide, without any alteration in the state of its combination: indeed it seems apparent that the action cannot be merely, if at all, a chemical one; for fragments of Trap and other rocks produce the same effect in the Devonshire red beds, and in the Old Red beds of Forfarshire (fig. 14, Plate XII.) and the red beds of the Grès des Vosges and of the Grès bigarré of the Vosges district (fig. 4, Plate XI.) fragments of various shales and rocks are concentrically surrounded by similar zones of bleaching.

The great majority of examples of variegation in which there are neither segregated nor mechanical nuclei exhibit similar conditions, viz. differences in the light and dark parts merely as regards the *proportion* of iron present, without any alteration in its state of combination, or change in the composition of the matrix.

The following analyses are of red Bunter sandstone, mottled

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* The

with pale blotches, &c., from a cutting on the Severn Valley Railway, between Linley and Bridgnorth, similar to those in fig. 41 from near Shiffnal.

Fig. 41.—Variegated Bunter Sandstone near Shiffnal, Shropshire.



Analysis No. 1, of the red ground, indicated

	Water of combination	0.65
	Sesquioxide of iron	1.30
	Alumina	0.80
	Lime	0.35
	Magnesia	0.75
	Insoluble siliceous matter, sand	96.31
		100.16
Analysis	No. 2, of the pale blotches, indicated	

	Water of combination	0.46
	Sesquioxide of iron	0.40
	Alumina	0.36
	Lime	0.26
	Magnesia	0.53
¥	Insoluble siliceous matter, sand	98.15

100.16

No important differences exist in the general composition of the red and bleached parts; and the iron occurring in both was almost entirely in a state of sesquioxide.

Sesquioxide of iron, in the light and dark parts of the Bunter Sandstone from the south of Bridgnorth, was found to be similarly proportioned :----

insoluble siliceous matter in No. 2 consisted of	
Alumina and traces of oxide of iron	1.97
Lime	0.42
Magnesia	
Silica	

100.25

[April 22,

Red Bunter, Analysis No. 23, by Dr. Voelcker, contained Sesquioxide of iron 1.84 per cent.

Grey blotches, Analysis No. 24, contained

Sesquioxide of iron 0.54 per cent.

The light and dark parts of mottled Cambrian grits, Bayston Hill, near Shrewsbury (fig. 24, Plate XIII.), indicated the following differences in the percentage of the colouring oxides of iron :---

Analysis No. 12. Light blotches and bands following the joints.

Protoxide of iron \dots 0.08Sesquioxide of iron \dots 3.00 Metallic iron 2.16.

The variegation resulted therefore from the departure of nearly two-thirds of the oxides of iron from the light portions without the state of combination of the remainder being much affected.

Of the states of combination, and of the proportions of iron in the light and dark parts of blotched red clays and marls, the following are examples.

Soft red clay mottled with buff, lying from 20 to 30 yards above the Sulphur-coal, Shropshire Coal-measures, Broseley.

Analysis No. 15, of the red ground, contained

 $\begin{array}{c} \textbf{Protoxide of iron.....}\\ \textbf{Sesquioxide of iron}\\ \textbf{Silicates of iron}\\ \textbf{0.15} \end{array} \} \textbf{Metallic iron 8.64}.$

Another analysis (No. 35) of the same clay indicated the presence of 7.54 per cent. of sesquioxide of iron, and traces of protoxide.

Analysis No. 16, of the buff blotches and seams in No. 15, contained

 $\begin{array}{ccc} \textbf{Protoxide of iron.....} & 0.90\\ \textbf{Sesquioxide of iron} & 4.20\\ \textbf{Silicates of iron} & 0.54 \end{array} \} \textbf{Metallic iron 4.01}.$

A determination of the iron of another example of the buff blotches (No. 16) was made at the laboratory of the Jermyn-Street Museum with the following result:—

which was present as

R

Sesquioxide of iron	1.81
Protoxide of iron, soluble	1
Oxides of iron insoluble,] 0.88	1.48.
weighed as protoxide	J

Red Permian marl, with buff blotches (Severn Valley Railway, near Linley station):---

ed marl (Analysis No. 4, Dr. Voelcker) con	itained
Sesquioxide of iron	3.23
Protoxide of iron	
Bisulphide of iron	0.02

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Buff blotches in red marl (Analysis No. 5) contained

Sesquioxide of iron	2.779
Protoxide of iron	1.468
Traces of sulphur.	

The general composition of the red and buff portions of the marl exhibited no material difference.

Buff blotches on red Permian marl (Analysis No. 22) contained

Oxides of iron, principally sesquioxide 3.67 per cent.

Red Marl, Old Red Sandstone, with buff blotches (roadside, Norley, near Bridgnorth):---

Red marl (Analysis No. 13) contained

Buff blotches on No. 13 (Analysis No. 14) contained

 $\begin{array}{c} \mbox{Protoxide of iron} & 0.54 \\ \mbox{Sesquioxide of iron, probably} \\ \mbox{hydrous} & \dots \end{array} \right\} 8{\cdot}60 \\ \end{array} \right\} \mbox{Metallic iron } 6{\cdot}44. \\ \end{array}$

The blotching of the red beds of the Wyre Forest Coal-field, Worcestershire (fig. 27, Plate XIV.), presents another phase of variegation, which is of frequent occurrence, viz. the bleached portions being adjacent to an overlying bed of sandstone, and branching out therefrom into the general mass of the underlying marl. As the disposition of the fields of colour is very suggestive of infiltration from the overlying beds in contact with the bleached marl, I have procured complete analyses of the red and the bleached portions.

The composition of the clay, railway-cutting near Bewdley, Worcestershire (fig. 27, Plate XIV.) was determined as follows, by Dr. Voelcker.

Analysis 1	No. 46 (re	ed). No. 47 (buff).
Water of combination	6.32	4.49
Sesquioxide of iron	12.21	3.44
Protoxide of iron	0.40	0.61
Bisulphide of iron	0.11	0.022
Alumina	17.57	5.33
Sulphate of lime	0.02	0.12
Lime in a state of silicate	0.71	0.71
Magnesia	2.22	0.73
Potash and soda	0.56	0.24
Insoluble silicates 60.29		84.35, including : —
Silica	50.23	65.30
Oxides of iron (weighed as sesquioxide)	1.19	1.59
Alumina	6·33	14.33
Lime	0.71	0.52
Magnesia	0.37	0.34
Alkalies and loss	1.46	2.27

1	0	n	•4	G

100.07

There is somewhat more alumina in the red than in the bleached part, and a much larger proportion soluble in hydrochloric acid; but this appears to be due merely to local variations in the composition of the clay, and to be unconnected with its variegation; otherwise the general composition of the red and bleached parts is similar, the main difference being in the small amount of sesquioxide in the buff (Analysis No. 47) compared with that in the red (Analysis No. 46) the amount of protoxide in the two colours being nearly identical, but slightly in excess in the buff portions. The change seems difficult to connect with infiltration from above, as isolated blotches of the buff occur entirely environed by the body of the red clay.

5. On Discoloration and Bleaching connected with Joints.—Variegation, which has evidently been more or less localized by the existence and position of cracks and joints, seems to be of several distinct kinds; one of which may be described as the simple rusting of the joint-surfaces in beds containing carbonate of protoxide of iron, and is evidently connected with surface-infiltration, for it always diminishes in proportion to the depth and distance from the surface. Fig. 20 (Plate XIII.) represents an example of grey marl that has become thus variegated; and fig. 22 (Plate XIII.) represents some beds of the Upper Purbeck marble, near Corfe, Dorsetshire. The contrast of colour between the blue centre of the slabs and the ochreous crust following the line of joints is very marked, but it is met with in some degree in all jointed beds containing protoxide of iron. This form of secondary variegation is_well explained by the following analyses, by Messrs. Johnson and Sons—

and is evidently due to the partial peroxidation of the carbonate of protoxide, there being but little difference in the amount of iron present. This example is particularly instructive, as bearing on the theory of the alleged dissolution of the colouring oxide to account for the bleaching of red beds: here is an extreme case of a bed charged with the least insoluble oxide of iron, under circumstances most favourable to its removal by dissolution; but instead of its solution, the iron along the joints has become converted into the comparatively insoluble sesquioxide, unaccompanied by any material diminution in its amount. Fig. 19 (Plate XIII.) represents a somewhat similar case of joint-rusting in the Great Oolite of Northamptonshire; but in this example the rusting not only follows the joints, but concentrically surrounds some isolated balls of clay; and it was probably induced by their hygroscopic property.

In contrast with the rusting of joints, the other form of jointvariegation must be noticed, viz. the bleaching of rocks that are coloured by the red sesquioxide along the lines of jointing. The

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first example is represented in fig. 42, of a vertical bleached line in the Bunter Sandstone between Linley and Bridgnorth.

The analysis of the Red Sandstone (No. 1) already given at p. 363, showed that it contained 1.3 per cent. of

sesquioxide of iron, whilst the bleached seam contained less than one-third of the amount, the general composition of the stones being otherwise similar.

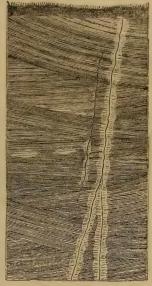
A rather different form of jointbleaching, analyses of which (Nos. 11 and 12, p. 364) have also been given, is represented in fig. 24, Pl. XIII., of chocolate-coloured Cambrian Grits, Bayston Hill, near Shrewsbury, in which the discoloured bands follow the intersecting lines of jointing both vertically and horizontally, often isolating the dark ground into oblong brickshaped forms, entirely surrounded by the bleached bands. In this the same process seems to have taken place as in the case of the Bunter, there being nearly two-thirds less iron in the light than the dark portions, with no material difference in the proportion of protoxide to sesquioxide, the insoluble sesquioxide being the condition in which it chiefly occurs throughout the rock. Now on looking at these

bleached lines ranging with the permeable joints, they appear at first sight due to some kind of solubility and washing out of the colouring-matter; but a careful examination shows that there is no essential difference between them and the isolated spherical blotches. In the vertical bleached lines in the Bunter (fig. 42), the discoloured line is here and there interrupted and broken up into isolated blotches. In the Cambrian grits of Shropshire (fig. 24, Pl. XIII.) every gradation occurs between the discoloured joint-lines and the completely separate bleached patches; indeed all these examples serve to show how capriciously the discolouring action has been localized—in some cases strictly following the joints, and in others branching out into irregular masses that have no reference to them.

In comparing these two forms of joint-variegation, viz. the rusting of beds charged with protoxide, and the bleaching of those coloured with the red sesquioxide, it seems difficult to assign to infiltration, which has failed to remove the more soluble carbonate of protoxide of iron in grey beds, the power of removing the comparatively insoluble sesquioxide of iron adjacent to the joints in red beds.

In considering the subject of the influence of organic matter in the bleaching of red beds, certain cases will be referred to in which the acids formed during the decomposition of organic matter appear to have acted as solvents of sesquioxide of iron; but the great majority of cases, in which bleached spots and joints occur in red VOL, XXIV.—PART I. 2 p

Fig. 42. Bunter Sandstone, Linley, near Bridgnorth.



beds, present features inconsistent with the mere dissolution of the colouring oxide.

The influence of joints, apart from their functions as channels of infiltration, will also be referred to in considering the phenomena of the banding of yellow sandstones (see p. 391).

There is also another singular form of banding influenced by the presence of joints, viz. in the rock-masses isolated by them. The banded purple and green beds of the Coniston Grits, represented in fig. 30 (Pl. XIV.), and in fig. 43, to which my attention was drawn by

Fig. 43. Banded purple and green Coniston Grits, Austwick, head of Crummuch-Water beck, Clapham, Yorkshire.



Professor Harkness and Dr. Nicholson, present the following characters. The whole mass of the rock is made up of concentric series of narrow purple and green bands, disposed without reference to the stratified structure of the rock, each nest of concentric bands being bounded by the main lines of jointing; for instance, in a triangular mass the bands concentrically follow its three sides, and in cubical portions have a square disposition, tending to curvilinear forms towards the centres. The finer cracks, which happen to die out and terminate in the middle of a mass, have also curiously influenced the direction of the banding, causing, as in fig. 30 (Pl. XIV.), a looping and deflection of the purple and green lines, as though a series of advancing lines had been arrested and held back where intersected by the joints, resulting in a structure resembling and, I believe, identical in principle with that of folded agates (see fig. 1, pl. xiii. vol. v. Geological Magazine, illustrating Mr. Ruskin's paper on "Banded and Brecciated Concretions"). The states of combination of the iron in each portion is given in the following analyses, made in the laboratory of the Museum of Practical Geology :---

Determination of iron in purple and green bands, Coniston Flags, Head of Crummuch-Water beck, Austwick, near Clapham, Yorkshire. The purple bands (Analysis 83) contained :---

Iron $\begin{cases} Soluble in hydrochloric acid 3.104 \\ Insoluble 0.566 \end{cases}$ Total 3.670 per ce	nt.
Insoluble	
Present as Sesquioxide of iron 1.347 per cent.	
Protoxide of iron	
Oxides of iron insoluble, weighed as protoxide 0.728	
Combined water 1.990	

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The green bands (Analysis No. 84) contained :---

Iron { Soluble in hydrochloric acid $2^{\cdot 232}$ Insoluble $0^{\cdot 502}$ } Total 2.734 per cent.
Present as Sesquioxide of iron 0.376 per cent.
Protoxide of iron 2.532 ,,
Oxides of iron insoluble, weighed as protoxide 0.648 ,,
Combined water 2.223 ,,

The rock therefore contained originally about 3 per cent. of iron, partly as sesquioxide and partly as protoxide and silicates; and the banding appears to be due to the segregation of the sesquioxide into the concentric purple layers, the green colour of the intervening courses resulting from the *exposure* of the green silicates and the protoxide, by the removal of nearly the whole of the obscuring sesquioxide.

Many jointed rocks exhibit this secondary concentric banding within each separate mass, bounded by lines of joint—some merely with respect to colour, by the rearrangement of the oxides of iron; but in others (for example, jointed granites and some Trap rocks, which exfoliate in concentric layers within each portion bounded by joints) there appears to have been a partial rearrangement of the mass of their constituents, and a corresponding modification of mechanical structure.

These curious phenomena seem to be more related to the *isolation* of the masses by the joints than to the mere fact of the jointing; for in waterworn stones the direction of the lines of secondary banding is often determined by the *contour assumed after separation* from the parent rock. In the case of flints banded with yellow and grey concentric layers of iron, in different states of combination, the bands range with the waterworn outline and not the original contour of the flint.

6. On the Variegation of the Keuper Marls.—The arrangement of the red and grey colours in the Keuper Marls is almost as capricious and anomalous as in some of the examples already referred to; and any satisfactory explanation is rendered difficult, on the one hand, by the disposition of colour being apparently related to stratification, and, on the other, by its being evidently the result of secondary causes. Fig. 13 (Pl. XII.) represents a portion of the section at Worcester station; its general aspect suggests that the alternation of the red and grey bands is simply the result of interstratification; but the interlacing outline at their junction shows that the grey beds are merely an altered condition of the red-isolated patches of grey breaking irregularly into the general red ground. There are also continuous grey beds, some of which are harder than, and of different mechanical composition from the red; and there are isolated patches of grey, which in general have a horizontal range, coincident with the stratification; but the recurrence of the individual blotches on their horizontal range is evidently determined by secondary causes. A portion of the beds included in the section are intersected by vertically disposed zigzag lines of hard stony matter, possibly repre-2 р 2

senting former cracks and channels of infiltration; and wherever they cross the horizontal lines on which the isolated grey patches occur, the particular position of each is evidently determined by the intersection of the hard seams along which the grey patch branches, as shown in fig. 44.

A somewhat similar case occurs in the red marls interstratified with the white Keuper sandstone in the Alderley copper-mine, Cheshire. Pockets or seams of the white sand occasionally run down from the sandstone into the marl (fig. 10, Pl. XI.), and adjacent to these seams the red marl is discoloured; and similar bleached marl bounds the line of separation of the red marl and sandstone-beds (fig. 11, Pl. XI.).

Fig. 44. Bleached patch in Keuper Marls, Railway Cutting, Worcester.



Again, the position of a grey patch amongst the red is frequently determined by a slightly harder condition of the stratum in a particular part. The variety of circumstances that have determined the position of these discoloured bands and blotches, and the variety in the character of the beds that are similarly affected, show that the phenomenon is quite independent of original differences in the chemical composition of the red and grey parts of the strata; this is confirmed by the following complete analyses of the red and grey parts of the Keuper Marls, Worcester Station, that have been made for me by Dr. Voeleker:—

No. 58, Red. No. 59, Grey. Water of combination. $4\cdot45$ $3\cdot71$ Protoxide of iron. $1\cdot60$ $1\cdot77$ Sesquioxide of iron $2\cdot41$ $0\cdot80$ Bisulphide of iron $0\cdot059$ $0\cdot029$ Alumina $11\cdot14$ $12\cdot77$ Lime $4\cdot85$ $3\cdot71$ Magnesia $3\cdot06$ $2\cdot17$ Potash $0\cdot69$ $0\cdot71$ Soda traces $0\cdot02$ Sulphuric acid $0\cdot09$ $0\cdot08$ Carbonic acid and loss $3\cdot311$ $4\cdot741$ Matter insoluble in hydrochloric acid : $4!0rina$ $9\cdot39$
Protoxide of iron. 1 ·60 1 ·77 Sesquioxide of iron 2 ·41 0 ·80 Bisulphide of iron 0 ·059 0 029 Alumina 11 ·14 12 ·77 Lime 4 ·85 3 ·71 Magnesia 3 ·06 2 ·17 Potash 0 ·69 0 ·71 Soda traces 0 ·02 Sulphuric acid 0 ·09 0 ·08 Carbonic acid and loss 3 ·311 4 ·741 Matter insoluble in hydrochloric acid :
Sesquioxide of iron 2:41 0:80 Bisulphide of iron 0:059 0:029 Alumina 11:14 12:77 Lime 4:85 3:71 Magnesia 3:06 2:17 Potash 0:69 0:71 Soda traces 0:02 Sulphuric acid 0:09 0:08 Carbonic acid and loss 3:311 4:741 Matter insoluble in hydrochloric acid :
Bisulphide of iron 0 0059 0 029 Alumina 11 14 12 77 Lime 4 85 3 71 Magnesia 3 06 2 17 Potash 0 69 0 71 Soda traces 0 02 Sulphuric acid 0 09 0 08 Carbonic acid and loss 3 311 4 741 Matter insoluble in hydrochloric acid :—
Bisulphide of iron 0 0059 0 029 Alumina 11 14 12 77 Lime 4 85 3 71 Magnesia 3 06 2 17 Potash 0 69 0 71 Soda traces 0 02 Sulphuric acid 0 09 0 08 Carbonic acid and loss 3 311 4 741 Matter insoluble in hydrochloric acid :—
Alumina 11·14 12·77 Lime 4·85 3·71 Magnesia 3·06 2·17 Potash 0·69 0·71 Soda traces 0·02 Sulphuric acid 0·09 0·08 Carbonic acid and loss 3·311 4·741 Matter insoluble in hydrochloric acid :— 1000 1000
Magnesia 3·06 2·17 Potash 0·69 0·71 Soda traces 0·02 Sulphuric acid 0·09 0·08 Carbonic acid and loss 3·311 4·741 Matter insoluble in hydrochloric acid :— — —
Potash 0·69 0·71 Soda traces 0·02 Sulphuric acid 0·09 0·08 Carbonic acid and loss 3·311 4·741 Matter insoluble in hydrochloric acid :—
Soda traces 0·02 Sulphuric acid 0·09 0·08 Carbonic acid and loss 3·311 4·741 Matter insoluble in hydrochloric acid :
Sulphuric acid 0.09 0.08 Carbonic acid and loss 3.311 4.741 Matter insoluble in hydrochloric acid :— 1.000 1.000
Carbonic acid and loss
Matter insoluble in hydrochloric acid :
Alumina
Silica
Oxides of iron weighed as sesquioxide 0.78 68.34 0.99 69.49
Lame
Magnesia 1.69 1.11
Alkalies and loss $\dots 2.22$ 1.66
100.00 100.00

The two examples contained but slight traces of carbonaceous

matter; and their general composition was identical, excepting as regards the iron, of which there seems to have been a departure of the greater part of the sesquioxide from the grey portion. The protoxide of iron in the grey is somewhat in excess of that in the red; but the difference is scarcely more than might occur in any two portions of the same stratum, and is insufficient to prove its secondary derivation from the red sesquioxide. The mottling of the Keuper Marls seems, therefore, in principle to differ in no respect from the blotchy variegation of other red clays and marls; and the two analyses of the Worcester example are worthy of note because they fail to exhibit the kind of change in the state of combination of the iron indicated by the analyses, given by De la Beche, of the Keuper beds at Aust Passage, viz. the reduction of the sesquioxide to protoxide without any departure of the iron.

7. On the Influence of Organic Matter in inducing Variegation.— The connexion between the blotching and discoloration of red beds and the presence of fossil carbonaceous and peaty matter has repeatedly been noticed by geologists, and reference has already been made to the observations of De la Beche on this subject in the Memoirs of the Geological Survey. The generally accepted theory, and that suggested by De la Beche in explanation of the phenomenon, is, that the discoloration has been brought about by the reduction of the sesquioxide to a lower state of oxidation of less colouring-power by simple chemical reaction with the fossil carbon. The experiments of Bischof, and also those of Kindler, published in Poggendorff's Annalen, establish the fact that sesquioxide of iron, by simple contact with organic matter, is capable of being reduced to a state of protoxide.

With a view to ascertain how far the reduction of the colour of red beds may be due to this process, I have procured analyses of the bleached and unbleached portions of a number of examples of ferruginous strata in which the variegation seems to be connected with the presence of fossil carbon.

The mottled beds of the Woolwich and Reading series, especially in their development as the Argile plastique of the Paris Basin, are particularly instructive in explaining the nature of the secondary disposition of ferruginous colouring as apparently dependent on accompanying organic matter.

Figure 45 represents a section at Vaugirard, Paris, from the Upper Chalk to the Calcaire grossier; the mottled beds of the Argile plastique (fig. 21, Plate XIII.) included in the section are overlain by 15 or 20 feet of grey laminated clays containing beds of impure lignite and pervaded throughout by carbonaceous matter. The gradation of this character downwards seems to be connected with the arrangement of the mottling of the underlying Plastic Clay. These beds include five distinct and well-marked colours, viz.:—

1st. The bright blood-red, which appears to have been the primordial tint;

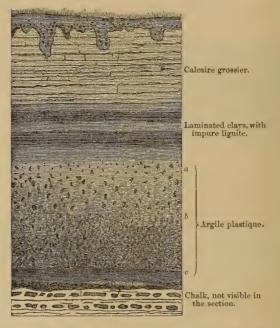
2nd. A light pinky red;

3rd. A dark brown;

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4th. An ochreous yellow; and, 5th. A light neutral grey.

Fig. 45.—Section of the Argile plastique and Calcaire grossier exposed in clay-pit, Vaugirard, Paris.



At the base (c), the blood-red primordial colour prevails with but slight variegation; towards the middle (b) the variegation becomes more definite, consisting of distinct patches of grey on the red or pink ground, each of which concentrically surrounds a nucleus of dark brown and red, as shown in fig. 21 (Plate XIII.), and is more or less mottled with ochreous yellow. As the carbonaceous beds are approached, the blood-red gradually dies out into neutral grey through intermediate shades of pink; and the uppermost portion (a)is variegated only by isolated brown blotches on a uniform grey ground, such as lower down formed the nuclei of the grey patches. The proportionate amount, and the state of combination, of the iron in these five shades of colour will help to explain the character of this curious and complicated variegation.

The blood-red portions of the clay, which are evidently in its primordial condition, contain :---

(Analysis No. 53, by Dr. Voelcker) Protoxide of iron	0.548	per cent.
Anhydrous sesquioxide	19.641	33
Organic matter	0.320	

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The ferruginous nuclei contain :---

(Analysis No. 55)	Protoxide of iron	0.474 per cent.
	(Hydrous) sesquioxide of iron 5	
	Organic matter d	loubtful traces.
	Water of combination	

The neutral grey zones immediately adjacent to the nuclei of segregation contain only about $\frac{1}{14}$ th of the proportion of iron in these centres, viz.:—

(Analysis No. 54)	Protoxide of iron	0.254 per cent.
	Sesquioxide of iron	
	Organic matter	slight traces.

The grey portions mottled with ochreous yellow contain :---

(Analysis No. 57)	Protoxide of iron	0.294 per cent.
	Hydrous sesquioxide	
	Organic matter	slight traces.

There is also the light-pink-coloured clay, through which the normal red graduates to the grey in the middle of the bed, and which occurs outside the grey zones surrounding the nuclei; and here we find the iron occurring in a proportion intermediate between that in the grey and that in the full red-coloured clay, viz. :---

(Analysis No. 56)	Protoxide of iron	0.254 per cent.
	Sesquioxide of iron	5.686 ,,
	Organic matter	0.790 ,,

Looking at these analyses, and the relative arrangement of the several colours, it is impossible to resist the conclusion that the excess of colour in the dark parts above the average composition, and its diminution in the adjacent light parts below the average, must be due to the actual passage of the iron to the centres of segregation. Here also, as in most other cases of segregation, the motion of the sesquioxide of iron is accompanied by its becoming hydrous, the blood-red of the ground being exchanged for a rich ochreous brown in the nuclei, and bright-yellow rust partially stains the exhausted portions. There is one point in connexion with the variegation of these mottled clays which seems difficult to explain satisfactorily, viz. the existence, about the ferruginous nuclei in the grey ground, of small patches of the blood-red clay quite unaltered, neither depleted nor enriched.

Among other cases of variegation apparently connected with the presence of organic matter, the following may be referred to. Fig. 25 (Plate XIII.) represents a yellow surface-clay containing fragments of black carbonaceous matter, adjacent to which the clay has been bleached of a pale-grey tint.

Analyses of the grey and yellow portions gave the following results :---

The yellow clay (Analysis No. 60, Laboratory of the Museum of Practical Geology) contained

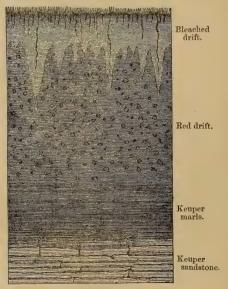
Total iron, Se	oluble	2.81] 2.55
" Í Iı	oluble	0.74 3.55 per cent.
Present as $\left\{ \right\}$	Sesquioxide of iron Protoxide of iron, soluble	3.20 ,, 0.74 ,,
[Sesquioxide of iron Protoxide of iron, soluble Oxides of iron weighed as pr.toxide} insolu	ble 0.96 "

The grey patches adjacent to carbonaceous matter (Analysis No. 61) contained

Fotal iron, Soluble 0.54 0.94 ,, Insoluble 0.40 0.94	per cent.
Sesquioxide of iron 0.16	
Present as { Protoxide of iron, soluble	,,,
Present as { Sesquioxide of iron	,,

Another, somewhat similar case is illustrated in fig. 46, of red surface loam (rearranged Keuper marls, in a railway-cutting between

Fig. 46.—Red Surface-loam, consisting of rearranged Keuper marls, in a railway-cutting between Codsall and Albrighton, Shropshire,



Codsall and Albrighton, Shropshire) intersected by seams and pockets of bleached grey loam, apparently connected with the penetration of roots from the surface.

The red loam (Analysis No. 67, Laboratory of Museum of Practical Geology) contained

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Total iron,	Soluble 2.46 Insoluble 0.23	2.69 per cent.
Present as -	(Sesquioxide of iron Protoxide of iron Oxides of iron weighed as protoxide}insoluble Carbon.	· 0·41 ,, • 0·29 ,,

The discoloured seams and pockets (Analysis No. 68) contained

Total iron, Soluble ,, Insoluble	••••••	$\left[\begin{matrix} 0.58\\ 0.15 \end{matrix} \right] 0.7$	3 per cent
Present as Sesquioxide of Protoxide of i Oxides of iro protoxide	f iron iron, soluble n weighed as $\}$ ins	0.5 0.2 oluble 0.2	55 ,, 25 ,, 20 ,,
Carbon	······	0.1	.14 "

The disposal of the oxides of iron which in this case have been withdrawn from the bleached portions is not evident; but in an example pointed out to me by Mr. J. W. Young, of Glasgow, the iron has been aggregated as hydrous sesquioxide into tubular concretions (fig. 47, a, b, c) concentrically disposed around roots penetrating the Post-tertiary clays about Glasgow, their transverse section (d) exhibiting a banded arrangement.

Fig. 47.—Concretions of hydrous sesquioxide of iron, Post-tertiary clays, Glasgow (actual size).

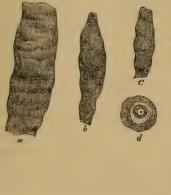


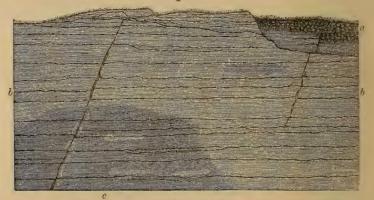


Fig. 48.—Bleached sand under peaty gravel. Cliff east of

In the cliff between Southwold and Easton-Bavent, in Suffolk (fig. 48), a surface layer of peaty gravel has bleached the brightyellow sands overlying the Chillesford clay to a depth of ten or twelve feet—the light-grey sands under the carbonaceous surfacelayer joining on to the golden-yellow sands in the bottom of the section with an outline not corresponding with the stratification.

In a Freestone quarry, Keuper Sandstone, Clive Hill, Shropshire (fig. 49), the bleaching effect of organic matter is again evident. In

Fig. 49.—Red, buff, and brown Keuper Sandstone, Clive Hill, Shropshire.



the top of the quarry dark-brown sandstone (a), spotted with creamcoloured blotches (fig. 40, Plate XV.), occurs with the following composition, determined by Dr. Vælcker :—

	Analysis Brown gr	NO. 62.	o. 63. Buff blotches on a.
Organic matter, humic and ulmic acids			0.31
Protoxide of iron, with traces of sesquioxide too small tobe separately determined	0.4	£2	0.32
Alumina		36	0.26
Lime	0.0)6	0.06
Sulphuric acid		80	0.07
Magnesia and traces of alkalies	0.2	26	0.34
Insoluble siliceous matter :			
	•44]	1.35	1
Oxides of iron	·31	0.30	j
Lime 0	47 } 97.6	30 0.43	>98.64
Magnesia and loss	08	0.19	1
	·30 j	96.37	J
	100.0		100.00
	100.0)0 =	100.00

The buff blotches were hard and crystalline, standing out from the weathered surface of the rock, and they may be segregations of silica; the colour of the brown ground is due to the presence of the organic acids. The bottom of the quarry exposes red sandstone (c), joining on with an irregular outline to the overlying mass of creamcoloured rock (b), the bleaching of which and loss of red colour appears, as in the case of the Southwold section, to be connected with infiltration from the uppermost bed charged with humic and ulmic acids.

A somewhat similar case is given in fig. 17, Plate XIII., of a specimen (in the Museum of the Jardin des Plantes, Paris) of a carbonaceous fossil in red Carboniferous sandstone at Ardenay, in which the colour immediately adjacent has been bleached.

The bleaching-power of carbonaceous matter is further illustrated in fig. 26, Plate XIII., of the Lower Green Sand near Folkestone,

where some carbonaceous spots are surrounded by discoloured zones, and these again concentrically surrounded by bright-yellow rings of hydrous sesquioxide of iron, which appears to have been displaced from the central area. Similar bleached patches frequently occur in the sands of the Crag district; and these, as in fig. 50, are always surrounded by a zone darker than the general colour of the sands, and coloured apparently by the iron withdrawn from the lighter area.

These phenomena present two distinct points for consideration :

-first, simple chemical reaction and the mechanical washing out of the iron in a soluble condition; secondly, the rearrangement of the colouring oxide, which cannot be explained by simple chemical and mechanical agencies.

Both of these processes seem to have operated in the production of those variegations of ferruginous strata which are connected with the presence of organic matter.

The Southwold, Clive Hill, and Codsall examples of bleaching appear to be the result of simple dissolution, and mechanical removal of the iron brought into a soluble condition. The generally accepted explanation, and that originally suggested by De la Beche, is, first, the reduction of the colouring-power of the iron by the conversion of the sesquioxide to protoxide, from deoxidizing contact with organic matter, and, secondly, the dissolution of the protoxide thus formed by carbonated water.

The experiments by Kindler and Bischof (Chemical and Physical Geology, vol. iii. page 1, English edition) establish the possibility of these reactions; but it is remarkable that in none of the cases that have been made the subject of the foregoing analyses does the bleaching appear due to *simple deoxidation*; and, furthermore, the proportion of protoxide to sesquioxide of iron is not increased in the bleached areas of red beds.

In grey beds accompanying carbonaceous deposits the iron is almost wholly in a state of carbonate of protoxide, and the nodules of

Fig. 50.—Bleached patch in yellow ferruginous sands accompanying the Crag, Wangford Crag-pit, Suffolk.



segregation are also carbonate of iron. Ferruginous nodules of segregation connected with the variegation and depletion of red beds, however, invariably consist of the sesquioxide. Carbonic acid *per se* is impotent in either reducing sesquioxide of iron to the lower oxide or in dissolving it. If, therefore, interbedded carbonaceous matter has operated as a solvent of sesquioxide in red beds by its reduction to protoxide, its effect must be limited to the parts in immediate contact; and it seems difficult to explain on this theory how, as in the case of the bleached beds at Southwold and Clive Hill, the operation can have extended to a distance of ten or twenty feet from the carbonaceous matter.

The direct solvent action of humic, ulmic, and other acids the product of organic decomposition, appears a more probable agent of dissolution, and does not necessarily involve the reduction of the sesquioxide to protoxide. According to Bischof (Chemical and Physical Geology, English edition, vol. i. p. 166), humic acid occurring in vegetable mould forms a compound with sesquioxide of iron soluble in 2300 parts of water and crenic acid, a combination soluble in ammonia. The formation of limonite or bog-iron-ore appears to be the result of such dissolution; it consists of sesquioxide of iron in combination with variable amounts of humic acid (Dana's System of Mineralogy, p. 178, fifth edition). The aggregation of sesquioxide of iron around roots and other vegetable remains in bogs may thus be incidental to its temporary dissolution by the acids of organic decomposition.

These simple chemical reactions, though coordinate with them, will not, however, fully account for such phenomena of variegation as those presented by the Argile plastique and Lower Greensand, in which the variegation has resulted not *from the loss of the iron in a soluble condition, but from its rearrangement,*—in the one case centripetally, resulting in its aggregation to concentrated nuclei surrounded by a depleted area; in the other centrifugally, the rearranged oxide of iron circumscribing the depleted area from which it was dispersed.

8. On Variegation due to the Decomposition of Bisulphide of Iron. —Among the secondary changes of colour from an altered state of combination, must be noticed that due to the oxidation of bisulphide of iron, which frequently occurs mechanically disseminated in sedimentary strata. Its simple oxidation, as is well known, results first in the production of sulphate of protoxide of iron and free sulphur, and ultimately, by the further decomposition of the protosulphate, of a rusty deposit of the hydrous sesquioxide. When iron pyrites occurs in mechanical association with grey beds charged with carbonate of protoxide of iron, as in the case of the London clay, the ultimate result of the decomposition appears to be limited to the production of the sesquioxide; but in a case which has come under my observation, a more complicated change appears to have taken place, involving the bleaching of beds charged with the anhydrous sesquioxide.

At the base of the Ashdown (Wealden) sands under the East Cliff, Hastings, occurs a bed of light bluish-grey tenacious clay, here and

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there tinged with red, and somewhat resembling in physical character the white Tertiary clays; but instead of burning of a light creamcolour in the kiln, the presence of much iron was indicated by the fire changing it to a dark yellowish-brown colour.

An analysis by Dr. Voelcker (No. 38) indicated that it contained nearly $1\frac{3}{4}$ per cent. of iron occurring as

Patches of pinky red in portions of the clay indicated the former presence of the iron in a state of anhydrous sesquioxide, which also occurs largely in the middle beds of the Wealden.

The partial decomposition of the pyrites, of which some still remains, seems to have brought about the discoloration. It appears that the whole of the sulphur of the decomposed pyrites has become oxidized, and has entered into combination with the ferric oxide, producing the neutral grey basic sulphate; and the original light-red colour of the bed has thus became partly obliterated. This is the only case of discoloration distinctly traceable to the decomposition of bisulphide of iron that has come under my notice; and few red beds contain a sufficient proportion of pyrites to convert by its decomposition the whole of the colouring sesquioxide into the almost colourless basic sulphate; but the case, though exceptional, should be recorded among the phenomena of variegation.

9. Variegated Cambrian Slates.—The variegation of Welsh slates, of which examples are given in figs. 29, 31, and 32 (Plate XIV.), and which seem to be the result of a combination of sedimentary and secondary causes, is of two kinds:—first, that consisting of well-defined blotches and bands disposed with more or less continuity, and always in harmony with the stratification; and, secondly, the conversion of the blue and purple slates to green, in contact with Trap dykes, and in large fields of colour interlacing irregularly with the normal colours, and disposed without regard to the stratification they vertically intersect.

These two forms of variegation appear to be due to independent causes.

The first case of stratified variegation (illustrated in fig. 32, Plate XIV.), when most fully developed, occurs in the form of interrupted green bands of two shades of colour, viz. dark olive-green layers of mechanical constitution different from that of the slate, and adjacent to them a zone of light-green discoloured slate, sometimes occurring on both the upper and under side, symmetrically enclosing the dark layer as a central nucleus, but frequently occurring only on the under side.

Having but recently described these beds in the Geological Magazine *, I need now only state that whatever may be the precise nature of the dark olive-green bands, it is evident they are of mechanical origin, and not the result of secondary segregation. Though often continuous for many yards, they are generally interrupted at

* Geological Magazine, March 1868, vol. v. p. 123.

intervals, and there exist all gradations between the continuous bands and isolated blotches.

These spherical bleached blotches generally contain a small nucleus of matter identical with that composing the dark-green layers, though not always visible, from the line of cleavage failing to intersect it.

The questions suggested by these phenomena refer to the time at which the bleaching took place. Was it before, or concurrent with, the slaty cleavage? and was the alteration of colour due to a change in the *condition*, or in the *amount*, of the colouring-matter? The first question is easily answered; for, as has been shown by Mr. Sorby, the form of the blotches has been notably affected by the cleavage attenuating them on the transverse section, whilst on the cleavage section they exhibit no distortion. I find also that the bands and blotches have partaken of all the movements affecting the slate, and are frequently broken by faults and dislocations. It is evident, therefore, that the bleaching was antecedent to, and independent of, the cleavage.

The composition of the discoloured spheres and bands adjacent to the green layers points to a conclusion respecting their character different from that arrived at by Mr. Sorby, that " they have been concretions of a peculiar kind, formed round bodies lying in the plane of bedding" (" On the origin of Slaty Cleavage," Edinburgh New Philosophical Journal, July 1853); for analyses of the purple and discoloured portions of the slate, which have recently appeared in the 'Geological Magazine' (vol. v. p. 123, March 1868), exhibit no material difference in general composition, and no aggregation of matter in the light parts that is not also found in the body of the slate; in short, they are identical, excepting that there has been a departure of about two-thirds of the sesquioxide of iron out of the bleached portions.

The blue slate, Glyn quarries, Llanberis (Analysis No. 45), contained

Sesquioxide of iron	5.68
Protoxide of iron	0.46

and the bleached bands underlying the dark-green layers (Analysis No. 44) contained

 Sesquioxide of iron
 1.59

 Protoxide of iron
 0.22

and appear to be precisely analogous to the discoloured spheres and bands in red beds. In these it has already been observed that matter of various kinds, as pebbles, fragments of stones, and fossils, has evidently induced and localized the motion of the colouring sesquioxide; so in the case of the banded slates, the layers of interstratified green matter appear to have similarly incited the departure of the sesquioxide of iron from the adjacent slate, without inducing any change in its state of combination. In the discoloured spheres of the segregated into small central nuclei; and it appears probable that the sedimentary green layers and spots to which the bleached slate is adjacent may have received as an accession the sesquioxide of iron abstracted from the surrounding zone.

The case of discoloured blotches from which the iron has been discharged, without any centre of aggregation, is more difficult to account for; but some examples of banded slates in the Penrhyn Quarries, given in fig. 31 (Pl. XIV.), seem to suggest an explanation; the light discoloured bands are concentrically surrounded by a dark band, darker than the slate, apparently by an excess of the colouring oxide, as though the oxide of iron had been dispersed centrifugally to the outline instead of aggregated to the centre; and it was observed that the mechanical layer forming the centre of the discoloured band is lighter in colour than where no such external dark zone occurs.

The other form of secondary variegation, viz. the conversion of the blue and purple slates to green in large fields of colour, and to green slate in contact with the intrusive greenstone dykes, appears to have no relation to that just described. An analysis (No. 29, by Dr. Voelcker) of an example from the Penrhyn Quarries showed that it contained 8.26 per cent. of iron, equivalent to 10.63 per cent. of protoxide as compared with (Analysis No. 27) 11.40 per cent. of sesquioxide in the purple slate of the same quarry. There is therefore no material departure of colouring oxide from the green variety, and we must look for an alteration in its state of combination to account for its change of colour.

The slates of a uniform green colour have no stratigraphical horizon distinct from that of the blue and purple varieties. The highest beds of slate in the Penrhyn Quarries (fig. 29. Pl. XIV.), underlying the uppermost Cambrian grits of Bronllwyd, and marked separately 10 and 11 in Professor Ramsay's section, No. 59 (p. 156, Geology of North Wales, Memoirs of Geological Survey), exhibit, on a large scale, this interchangeable colouring. The highest portion of No. 11 is more generally green, and purple prevails in No. 10; but there is no distinct line of demarcation between the two colours, which interlace with each other in a direction vertical to the stratification.

The purple (Analysis, No. 27) contained

Protoxide of iron	0.874
Sesquioxide of iron	6.540
Sulphur	0.031

The green (Analysis, No. 28) contained

Protoxide of iron	• • • • • • • • • • • • • • • • • • • •	5.49
Bisulphide of iron		0.15

A second analysis of No. 28 gave 5.90 per cent. of protoxide of iron. The change of colour is therefore due to the conversion of the sesquioxide of iron into protoxide; there was also about onesixth less iron in the green than in the purple, a difference insufficient to explain the change of colour, but accounted for by the fact that the green slate contains local deposits of segregated iron as crystallized pyrites.

An example of green slate, converted from the purple in contact with a dyke of diabase, Dinorwic Quarries, Llanberis (Analysis No. 52), contained

Protoxide of iron	. 5.568
Sesquioxide	. 3.133
Sulphur	0.011

Under the microscope the protoxide of iron appeared to occur as chlorite. The production of great masses of green slate can therefore be explained by a simple chemical process, viz. the partial reduction of the sesquioxide to a state of protoxide, and the separation of a small proportion as bisulphide rearranged as distinct crystals. The green banding of the Cambrian slates, and the production of the large uniform masses of green, were therefore not only due to independent causes, but occurred at different times,—the banding and blotching before the slate was cleaved; and some of the green slate was converted from the purple at the time of the intrusion of the greenstone dykes, which Professor Ramsay regards as of Post-carboniferous age.

10. On the Discoloration of Red Beds by Lime and Magnesia.— The absence of red beds from strata that are interstratified with calcareous bands, and the general absence of calcareous matter from red beds, must be noticed in connexion with the following examples of secondary variegation, which seem to be connected with the presence of carbonate of lime.

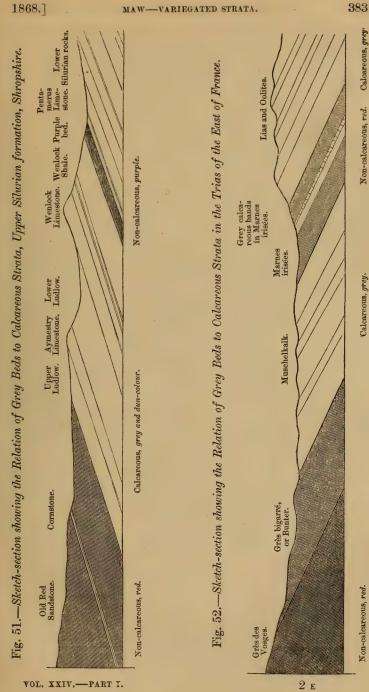
De la Beche, at page 53 of vol. i., Memoirs of the Geological Survey, notices that many of the green and blue bands in the red marls of the Old Red Sandstone of Herefordshire were found to be calcareous, or half-developed cornstones. With this exception, the large extent of non-calcareous *red* rock of the Old Red Sandstone forms a striking contrast with the great thickness of Upper Silurian *dun-coloured* beds that underlie it, and in which the calcareous element prevails. This is expressed in fig. 51, exhibiting an entire absence of red beds, from the top of the Ludlow rock to near the base of the Wenlock shale, where a reddish-purple bed appears.

This fact is not accounted for by the absence of ferruginous matter, as the Wenlock and Ludlow dun-coloured shales contain as much iron as the Devonian red beds above, and the purple bed below. It seems, however, to be directly correlative with the presence of carbonate of lime. In Shropshire the proportion of lime gradually increases upwards, from the purple bed as a minimum, at the base, to the massive limestone as a maximum, at the summit of the Wenlock beds.

An analysis (No. 51) of this purple bed at Minton, near Little Stretton, shows that it contained

 $\begin{array}{c} \mbox{Protoxide of iron} & 0.72 \\ \mbox{Sesquioxide} & & 7.70 \\ \mbox{Insoluble oxides} & & 0.75 \end{array} \} \mbox{Metallic iron 6.27,} \label{eq:sesquioxide}$

and about $7\frac{1}{2}$ per cent. of carbonate of lime.



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This purple bed scarcely occupies a distinct stratigraphical horizon, but passes upwards, with a blotchy interposition, into the great mass of overlying dun-coloured beds.

An analysis (No. 50) of these from between Harley and Much Wenlock indicated the following composition :---

Protoxide of iron 1.80

Sesquioxide of iron 7.00 Insoluble oxides of iron . 0.35

with about $9\frac{1}{2}$ per cent. of carbonate of lime, besides calcareous nodules of segregation.

There is no material difference in the amount of the iron : the sesquioxide in the purple bed appears to exist as the anhydrous form, and that in the dun-coloured beds as the hydrous; and the proportion of protoxide to sesquioxide increases upwards with the increase in the amount of calcareous matter, until in the blue beds of the Wenlock limestone the iron exists principally as carbonate of protoxide. The relation of this dun-colour to the presence of lime is further supported by the fact, that where the calcareous Pentamerus-zone appears between the purple bed and Llandovery conglomerate, it is accompanied by dun-coloured, and not purple shales, and where the band of Woolhope limestone appears in Herefordshire on the horizon of the purple bed in Shropshire, the purple colour is lost. The same principle appears to hold good with respect to the distribution of colour in the Trias of the east of France, a sketch-section of which is given in fig. 52.

In the neighbourhood of Lunéville, near Nancy, the red colour of the Marnes irisées disappears in descending to the Muschelkalk, the calcareous bands being interstratified with grey marls; and again, when the Muschelkalk is passed, and the calcareous element goes out, the red colour reappears in the Grès bigarré or Bunter. The same relation of colour to calcareous matter is observable within the Marnes irisées, and is illustrated in fig. 15 (Pl. XII.), representing a section at Enville near Lunéville, in which the change of colour from red to grey seems to have been induced by the presence of bands of magnesian limestone. Immediately adjacent to these the marl is of a uniform grey colour, and the underlying red colour begins to come in as small isolated spots and lines; these gradually increase in proximity until they graduate, through a red ground freckled with grey, into the mass of the uniformly red marl.

The following analysis by Dr. Voelcker gives the composition of the interstratified calcareous layers, and of the red and grey parts of the Marnes irisées at Enville near Lunéville.

Analyses.	No. 69. Red marl.	No. 70. Grey marl.	No. 71. Hard band.
Water of combination	4.24	3.97	1.73
Bisulphide of iron	0.02	0.037	0.025
Protoxide of iron	0.82	0.64	0.45
Sesquioxide of iron	4.93	1.90	1.13
Alumina	10.16	13.22	4.32
* Lime	10.59	19.38	27.16
	No. 69.	No. 70.	No. 71.
* Equal to Carbonate of Lime	18.92	34.62	48.51

Analyses.		lo. 69. d marl		No. 70. rey marl.	No. 71. Red band.
* Magnesia		8.96		7.60	18.52
Potash		0.76		0.13	0.42
Soda		0.12		0.02	0.09
Sulphuric acid	1	none.		none.	0.13
Carbonic acid and loss	1	5.86		22.763	36.765
Insoluble siliceous matter :					
Silica 36	5.72)		26.54)	
	-35		2.83		
)•15 (]	13.51	0.30	30.34	9.26
	P43 [1	10 01	0.23	10001	mostly Silica.
	-53		0.36	1	
Alkalies and loss 1	.•33 /		0.08)	
	10	00.00	1	00.00	100.00

In this section the change of colour seems to have been brought about by a combination of mechanical and secondary causes. The amount of iron decreases upwards from the red to the grey beds; but the curious freckled disposition where the grey and red colours interlace is evidently not the result of sedimentary arrangement, and appears to be connected with the infiltration of lime from the overlying calcareous bands, and a secondary bleaching of a uniformly red bed. Fig. 16 (Pl. XII.) represents a section of some Permian strata in a cutting of the Severn Valley Railway, between Linley and Bridgnorth, including red marls overlain by a calcareous band, in contact with which the red marls have been discoloured of an ochreous grey; the interlacing disposition of the yellowish grey and the red, with an irregular boundary of separation, shows that the former is a secondary product of the original uniform red colour.

The composition of the red marl (Analysis No. 4, by Dr. Voelcker) is as follows :----

Water of combination	2.79
Sesquioxide of iron	3.23
Protoxide of iron	1.35
Bisulphide of iron	0.02
Carbonate of lime	4'15
Sulphate of lime	0.17
Alumina	3.95
Magnesia	2.17
Alkalies and loss	1.22
Matter (exclusive of the iron) insoluble in hydro-	
chloric acid	80.95
	100.00

The composition of the ochreous yellow marl (Analysis, No. 3, by Dr. Voelcker):--

Water of combination Sesquioxide of iron Protoxide of iron Sulphur			0.309
* Equal to Carbonate of Mag-	No. 69.	No. 70.	No. 71.
nesia and Magnesia in a state of	14.40	14.36	28.43
silicate	2.10	0.76	4.41

Carbonate of lime	35.58
Magnesia	
Alkalies and loss	0.35
Alumina	2.44
Matter (exclusive of the iron) insoluble in hydro-	
chloric acid	52.51
	100.00

The principal difference in the composition of the red and ochreous portions consists in the presence of a large proportion of carbonate of lime in the latter, which has evidently been infiltrated from the overlying calcareous band, accompanied by a change to the colour prevailing in the more calcareous parts of the Wenlock shale. In this case, however, there is no increase in the proportion of protoxide to sesquioxide of iron. The yellow colour of the Magnesian Limestone lying in the midst of red beds, may perhaps be an analogous case; and the entire absence of red beds from the calcareous Oolites must also be noticed; it is clearly independent of the amount of iron present, as nearly all the grey and yellow beds of the Oolites (see analyses Nos. 64, 65, 66, p. 357) contain similar proportions of iron to those in the various red beds.

Although an increase, from extraneous sources, of the calcareous element in any red bed seems to induce bleaching and discoloration, it does not bear a perfectly regular ratio to the proportion of lime present, as discoloration has taken place in some red beds connected with the infiltration of a less amount of carbonate of lime than that originally present in others that have not been so changed, and a blood-red colour pervades the base of the chalk at Hunstanton. It may, however, be generally stated that a bright-red colour is a character of non-calcareous strata, and dun-colour, or grey, of calcareous beds, quite irrespectively of the amount of iron present.

I will not attempt any explanation of these facts, and merely offer them as worth further investigation, and requiring a larger series of observations before any reliable conclusions can be suggested.

11. On the Condition of the Iron in the Depleted Areas of Red and Purple beds.—Before leaving this part of the subject special reference must be made to the circumstances attending the colour and state of combination of the iron in the buff and green blotches of slates and red beds. It is important to bear in mind that their colour bears no definite relation to the proportion of the iron which they contain. As a rule the blotches contain a much smaller proportion of iron than the red, purple, or blue ground on which they are disposed; but whilst a certain proportion of iron may form the colouring base of one red bed, it may contain actually less than the light blotches on another; and, furthermore, the great bulk of the iron may in each case be in a state of sesquioxide; so that the mere abstraction of a part of the iron will not by itself explain the local reduction of the red eolour to a paler hue.

The discoloured blotches vary in tint from a light clear sea-green

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to an ochreous yellow. Although these extremes are not very distinct, and are connected by a series of gradations of intermediate shades of colour, they are evidently due to independent causes. There seems to be no uniform relation in the proportion of silicate of iron in the light and dark parts of variegated beds; and its amount seems to vary independently of the action of discoloration. The protosilicate is probably the colouring principle of the blotches tending to green. Bischof (Chemical and Physical Geology, vol. ii. p. 130, English edition) also records the occurrence of this green protosilicate in variegated sandstone which had no green colour. In association with sesquioxide of iron, the green-colouring power of the silicate would be obscured, but developed on the removal of the red sesquioxide. This, we have seen, has taken place in every degree; and where the segregating motion of the red anhydrous sesquioxide has occurred, it has generally become hydrous. The hydration of itself, without any diminution of the sesquioxide, would produce a lighter yellow blotch on the red ground; indeed, in the red clays of the Lower Bagshot beds, a yellow clay occurs, lighter in colour than the red, though containing more of the sesquioxide of iron, and rendered lighter simply by its becoming hydrous.

The following are analyses of the red and yellow portions of the variegated clay represented in fig. 23, Pl. XIII.

Analysis No. 33. Blood-red clay, Lower Bagshot beds. Messrs. Pike's Clay Works, Wareham. (Dr. Voeleker.)

Sesquioxide of iron with traces of protoxide ... 5.28 per cent.

Analysis No. 19. A second specimen of bright-red clay, Messrs. Pike's Clay Works, Wareham, Lower Bagshot beds. (Laboratory of the Museum of Practical Geology.)

Total iron	Soluble	2.52]	per cent.
Present as	(Sesquioxide of iron	2.944	**
1 1050110 46	Oxides of iron, insoluble, weighed as protoxide	0.590.	

Analysis No. 20. Bright ochreous yellow clay, intermixed with No. 19. Lower Bagshot beds, Messrs. Pike's Clay Works, Wareham. (Laboratory of the Museum of Practical Geology.)

Total iron	$ \left\{ \begin{array}{ll} \text{Soluble}5382 \\ \text{Insoluble}0361 \end{array} \right\} $	5.743.
Present as	(Sesquioxide of iron	7.69,
	weighed as protoxide	0.465.

The variegation of the Horderley (Caradoc) sandstone, fig. 28 (Pl. XIV.), in which green bands and blotches occur on a purple ground, appears only accountable by the further hydration in patches of the sesquioxide of iron to which the purple colour is due.

The following determinations of the iron in the purple and green portions fail to afford any other explanation, as they contain identical amounts of sesquioxide.

5.37

87.35

100.00

idstone, Horderley, Shropshire.	
Water of combination	0.42 per cent.
Soluble { Protoxide of iron	1.11
Soluble Sesquioxide of iron	3.51
Alumina and other constituents	
soluble in hydrochloric acid	2.47
Insoluble siliceous matter con-	
taining oxides of iron, weighed as sesquioxide 1.055	92.49
as sesquioxide 1.055	
	100.00
Analysis No. 88, by Dr. Voelcker. Green J	portion.
Water of combination	1.29 per cent.
Soluble { Protoxide of iron	2.48
Sesanioxide of iron	3.51

Alumina and other constituents soluble in hydrochloric acid

Insoluble siliceous matter con- } taining oxides of iron, weighed }

as sesquioxide 0.668

Analysis, No. 87, by Dr. Voelcker. Purple portion, Horderley sandstone, Horderley, Shropshire.

In the green part of this example there is an excess of protoxide, compared with that in the purple, without a corresponding diminution in the soluble sesquioxide, though the total amount of iron is nearly equalized by the excess of insoluble oxides of iron in the purple.

There are, therefore, two distinct causes operating together in determining the colour of the pale blotches in red beds and slates first, the *exposure* of the pre-existing green protosilicate by the partial or entire removal of the red sesquioxide, and, secondly, the conversion of any remaining anhydrous sesquioxide into the hydrous form.

The higher silicates, which tend to a yellow colour, may also be in part the colouring-matter of the depleted blotches. Their separate determination in the analyses has not been attempted; and it is sufficient for my present purpose to observe that they are numerous, that their constitution varies with their occurrence, as double silicates with lime, magnesia, &c., and that their colours range from green to yellow.

12. On the Ferruginous Banding of Yellow Sandstone.—Another form of variegation, distinct from those before referred to, is seen in the arrangement of hydrous sesquioxide of iron in yellow strata, as bands and fields of colour disposed unconformably to the stratification.

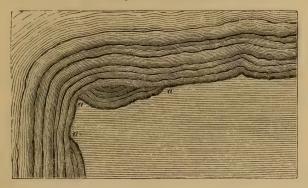
That this ferruginous banding is independent of the original mechanical arrangement is obvious; and the question it suggests is, whether the variegation results from the infiltration of the iron on to a light ground, or from a rearrangement of the yellow sesquioxide originally pervading it.

In some cases, as in fig. 53, the disposition of the ferruginous lines bears a resemblance to the way in which a coloured liquid stains and pervades an absorbent body (for example, stains of coffee

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on a linen cloth), the circumference of the patch being darker than the general mass, and drying up to a hard line against the unstained

Fig. 53.—Carboniferous Sandstone, with Ferruginous Bands, Workington, Cumberland.



portion. I believe the similarity is only resemblance, and that a careful examination of the whole of the phenomena presented by banded yellow rocks will lead to the conclusion that it is independent of any mechanical process.

One of the most suggestive points is the almost invariable contiguity of the lightest to the darkest parts of the strata. In some cases dark ferruginous bands are environed on either side by exceptionally light portions, which graduate into the general colour of the stone; but the most frequent arrangement is the bounding of the dark band on one side by white sandstone, and on the other by yellow.

On any view of mere mechanical arrangement it is impossible to explain this very constant phenomenon, as, if the ferruginous stain was infiltrated into a lighter-coloured rock, the presence of exceptionally light portions, *lighter than the average colour of the bed*, seems quite unaccountable.

Fig. 35, Pl. XV.*, and figs. 54 and 55, represent two of the simplest forms of this banding and blotching—figs. 35 and 54 consisting of isolated light patches on a uniform yellow ground, separated by a dark ferruginous ring, and fig. 55 of a yellow patch separated by a similar ferruginous band from the lighter ground on which it is placed. In this case the complete isolation of the dark areas of ferruginous colour excludes the possibility of their being due to foreign infiltration. Fig. 56 represents a somewhat similar form of variegation, occurring in the Ashdown sands (Wealden), near Hastings; and determinations of the iron in the light and dark portions, made at the Labo-

^{*} I wish to express my obligations to Mr. Allen for the very successful execution of Pl. XV. by the mezzotint process, which seems peculiarly available for the rendering of subjects with much variety of colour. The whole of the colours on this sheet were worked from two steel plates, with only two separate printings.

Fig. 54.-Banded Yellow Rock, Northamptonshire Oolites.

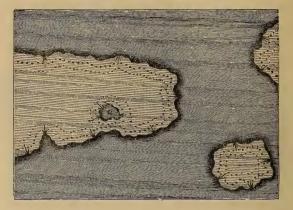


Fig. 55.—Banded Sandstone, Grès des Vosges, near Raon l'Etape, Vosges.

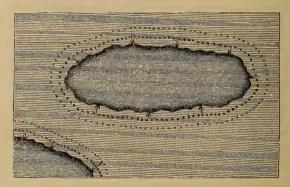
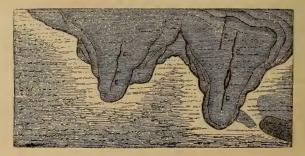


Fig. 56.-Variegated Yellow Sandstone, Ashdown Sands, Hastings.



ratory of the Museum of Practical Geology, gave the following results :---

Analysis No. 89. Light ground, Ashdown Sands, near Hastings (fig. 56).

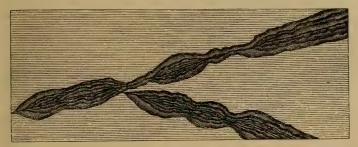
Iron { Soluble in hydrochloric acid	$\begin{pmatrix} 0.130\\ 0.095 \end{pmatrix}$ Total 0.225.
Present as Sesquioxide of iron	0.145
", Oxides of iron, insoluble, weighed as pro- toxide	
L . N . OO . Willing anothing of Ashdo	

Analysis No. 90. Yellow portions of Ashdown Sands, near Hastings (fig. 56).

Soluble in hydrochloric acid Insoluble	$\begin{pmatrix} 0.911 \\ 0.086 \end{pmatrix}$ Total iron 0.997.
Present as Sesquioxide of iron , Protoxide of iron	
", Oxides of iron, insoluble, weighed as protoxide	0.111

The dark area in fig. 56 contained therefore about four times the amount of iron in the light; and the dark ferruginous band of separation (of which no determination was made in this example) would contain from 30 to 40 per cent of hydrous sesquioxide of iron. The position of the cracks, c, c, in relation to the darker area is strongly suggestive of infiltration; and a somewhat similar arrangement of ferruginous colour, in relation to lines of joints, occurs in the Carboniferous sandstone on the coast south of Whitehaven (fig. 57).

Fig. 57.-Carboniferous Sandstone, coast south of Whitehaven.



Some of the jointed rocks (fig. 58), however, on the same coast, in which the disposition of the light and dark areas is evidently related to the joints, present the very reverse arrangement—the light areas bounding the lines of joining, whilst the general yellow ground occupies the intervening spaces.

Here, therefore, there appears to be the same kind of interchangeable arrangements of light to dark, and dark to light, as is found in the other forms of variegation, the exhausted areas being the result, not only of aggregation, but of dispersion, and corresponding with the examples figs. 54 and 55, in which both an isolated depleted area occurs on a darker ground, and isolated dark areas on a light depleted ground.

Fig. 58.—Carboniferous Sandstone, coast south of Whitehaven.



The arrangements of yellow banding generally occur quite irrespectively of the mechanical structure of the bed, the stratification being indifferently intersected by it. In other cases, variations of mineral structure seem to have influenced similar rearrangements of the oxide of iron, e.g. the presence of pieces of clay in the Ashdown Sands, Hastings (Pl. XV. fig. 33), having determined the aggregation of a shell of oxide of iron around them, accompanied by the bleaching of the surrounding sandstone. In another case, lenticular patches of sandstone in the midst of a more clavey bed has determined the aggregation of the ferruginous line to the point of separation.

In some parts of the Ashdown sands, at the foot of the East Cliff, Hastings (fig. 59), a further

change has supervened, the connected Fig. 59.-Ashdown Sands, banding having given place to the separation of the oxide of iron into small nuclei, the disposition of which faintly indicates the original continuous lines. Nearly all yellow strata coloured with the hydrous sesquioxide of iron give indications of these secondary changes. The Calcaire grossier (Pl. XV. fig. 34) is occasionally faintly banded; and wherever a line occurs darker than the general creamcoloured ground, it is invariably accompanied by an adjacent line somewhat lighter. Although these bands

Wealden, Hastings.



range with the stratification, they can scarcely be due to mere mechanical alternation; and the darker accumulations seem to have resulted from the impoverishment of the adjacent bleached portions.

Whatever may have been the active agent which brought about these changes of position, the kind of motion which has rearranged the oxide of iron may be suggested by the facts before us. Instead of its direct accumulation into spherical nuclei as in most red beds, the separation seems to have taken place in lines which have advanced in one direction, leaving behind them the bleached sandstone deprived of its iron, and gradually gathering up the iron in its advance. This motion has sometimes taken place in the plane of stratification (Plate XV. fig. 34), and sometimes centripetally, either towards some mechanical nucleus, which it has ultimately environed and closed over with a ferruginous crust (Plate XV. fig. 33), or in the body of the homogeneous stratum, enclosing, as in fig. 55, p. 390, an isolated portion of the unaltered yellow sandstone. More rarely the motion has taken place centrifugally, the lines expanding from the series of centres (Pl. XV. fig. 35, and, suprà, fig. 54), ultimately leaving isolated exhausted patches, circumscribed by spherical cakes of oxide of iron, and lying in the midst of the unaltered ferruginous matrix.

In the Wealden and Keuper sandstone these lines of segregation are often disposed with a very complex arrangement, one ferruginous band abruptly terminating at right angles to a horizontal or concentric series. The lines never cross each other; and one series appears to have absorbed (as in fig. 36, Pl. XV.), and rearranged on its own line of disposition, the

oxide of iron from the lines it Fig. 60. - Yellow-banded Carbonisuperseded.

There are cases, as in fig. 60, of banded Carboniferous sandstone at Benthall, near Broseley, in which a number of concentric lines of ferruginous segregation appear to have simultaneously advanced and closed in towards a centre. producing an alternation of brown bands of accumulation, and bleached bands of depletion, the lightest and darkest parts being always in juxtaposition.

ferous Sandstone, Benthall, near Broseley.

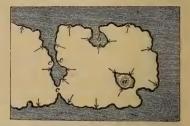


Another point to be noticed is the occurrence, within the light areas of depletion, such as are represented in figs. 53, 54, 55, 58, and 61, of isolated patches of the unaltered yellow rock, circumscribed by the ferruginous line of accumulation. In these cases the ferruginous line bounding the mass of the depleted area is very sinuous, apparently from an irregular rate of advance at different points. The outer yellow ground may thus intersect the depleted area by deep bays (b, fig. 61); and these, by the continued irregular advance outwards of the absorbing line, may become isolated and left behind, like islands (a, fig. 61) in the depleted area. There is also another cause for this phenomenon ; the sinuous circumscribing line

of two neighbouring areas of depletion, in their centrifugal advance,

will ultimately coalesce (as near the bottom of fig. 37, Plate XV.) at the first point of contact, and thus isolate portions of the yellow ferruginous ground, as in fig. 61, c, c.

The further encroachment of the line of accumulation over the detached patch will then be convergent, though it is simply an uninterrupted continuation of the divergent course of the main line. This may perhaps help to explain the apparently opposite Fig. 61.—Direction of Line of Ferruginous Accumulation in banded yellow Sandstones.



courses that the absorbing lines have taken under similar conditions; the kind of motion is the same in both cases, the uniform tendency being for the line of accumulation to advance from the already exhausted area towards the unexhausted part, whether it be a centrifugal or centripetal motion.

This yellow banding, represented in fig. 36, Plate XV., is so evidently connected with the contiguity of mineral veins, that it may be important to notice the precise manner of its occurrence. The Lower Keuper of Shropshire consists, for the most part, of light-buff sandstone, brown-mottled sandstone (fig. 40, Plate XV.), before referred to (p. 376), red sandstone, scarcely distinguishable from the underlying Bunter, and the curiously banded yellow sandstone, fig. 36 (Pl. XV.). These do not occupy distinct stratigraphical horizons. The red and buff series of rocks is vertically intersected by copper-lodes* of a bright sea-green colour, for the most part devoid of iron. The sandstone, which at a distance from the lode is red and buff, is, where it forms its boundary, charged with hydrous sesquioxide of iron, arranged in fine bands. The ferruginous lines end irregularly and abruptly against the lode-like mass of sandstone charged with copper, the boundary being generally defined by a thin brown line of hydrous sesquioxide of iron, into which the other ferruginous courses coalesce. The presence of this "cordurov rock" is looked upon by the miners as a sure indication of proximity to the copper; and as the lode is horizontally receded from, the sandstone assumes its ordinary red-and-cream colour.

Looking, then, at the fact that the light beds of the Keuper are both underlain and succeeded by great masses of red beds, and that they include isolated patches of red rock vertically disposed through their mass, and much iron in a variety of conditions and modes of arrangement on every horizon, their uniformly primordial red colour seems probable; and the evident connexion between the variegation

^{*} These are not true lodes with a distinct filling to the matrix, but consist of the ordinary sandstone charged with from 1 to 5 per cent. of carbonate of copper, and containing also cobalt, manganese, baryta, lead, &c., the whole having a lodelike disposition vertically intersecting the adjacent rock.

of these beds and the occurrence of mineral veins may perhaps help to throw some light on the agency by which the rearrangement of the iron has been influenced.

Another peculiar form of variegation occurring in the Keuper Sandstone, and due to the secondary disposition of copper and iron, is represented in figs. 38 & 39, Plate XV., from the Alderley coppermine, and consists in the segregation to distinct points, out of a common ground, of carbonate of copper and hydrous sesquioxide of iron. These examples give evidence of a dispersive as well as an aggregating action; for round each nucleus of copper there is a pale circumscribing zone from which the iron has been expelled. The iron appears also to have occupied particular centres, from which the copper has in like manner been driven, resulting in a singularly picturesque mottling of brown and blue blotches, with interspersed gradations of green and yellow.

13. The Variegated Iron-ore Deposits of the Northamptonshire Oolites.—In connexion with the subject of yellow-banded sandstones, reference must be made to the ironstone deposit of Northamptonshire, which illustrates with strongly marked features the same principle of arrangement. A position has been assigned to it both at the base of the Great Oolite and the top of the Inferior Oolite. The workable bed averages from 12 to 20 feet in thickness. Fig. 37 (Plate XV.) represents a portion from the neighbourhood of Blisworth, compiled from a sketch made on the spot, and some photographs kindly procured for me by my friend Mr. S. Sharp, F.G.S., of Dallington Hall. The whole stratum gives indications of having been completely rearranged since its deposition, even to the almost entire obliteration of its stratified structure.

Taking the bed *en masse*, it contains, averaging one part with another, from 25 to 40 per cent. of iron. It consists, for the most part, of a loose earthy friable ground of a bright-yellow colour, exhibiting an oolitic structure under the microscope. Its composition is as follows :---

No. 79. Analysis by Dr. Voelcker of a friable portion of the Northamptonshire iron ore, near Blisworth :---

Protoxide of iron	0.875
Sesquioxide of iron	21.280
Phosphoric acid	
Sulphuric acid	
Silica, lime, alumina, magnesia, &c,, not separately determined	
Carbonic acid	none.

This was pervaded by hard ferruginous bands having, for the most part, a curious cellular arrangement, with the same disposition as the structure represented in fig. 54; but, instead of occurring at isolated intervals on the yellow ground, the entire mass of the stratum is made up of the box-like structures. From mutual pressure in close proximity they have assumed the forms of irregular cubes, sometimes elongated in harmony with the stratification, but occasionally, where a joint appears to have occurred, attenuated in a vertical direction. It is important to notice that the boundary of each cavity is independent and complete in itself, so that the hard septa separating the cubes are *double*, and may generally be parted into distinct layers (fig. 62). The following determination of

the iron was made by Dr. Voelcker.

Analysis No. 78, of hard ferruginous cakes and layers, Northamptonshire iron-ore deposit, near Blisworth :---

Protoxide of iron	1.352
Sesquioxide of iron	76.538
Phosphoric acid	0.020
Carbonic acid	0.014
Silica, alumina, lime, water, &c., not separately deter- mined.	

Fig. 62.—Detail of Structure of the Oolitic Iron-ore formation, Northamptonshire.



These bands of accumulation appear to have originated in the same way as the dark lines represented in fig. 54, p. 390, each having advanced from its centre until arrested by contact with its neighbour, mutual pressure against each other having determined the angular form of the ferruginous shells.

In addition to the yellow earthy ground forming the mass of the deposit, and occupying most of the cavities, two other conditions of iron are found. At about the middle of the bed occurs a line of grey nodules of compact carbonate of iron, each of which is environed by a cellular crust of the hydrous sesquioxide; their composition is as follows.

Analysis No. 76, by Mr. D. Forbes, of nodules of compact carbonate of iron (upper part of fig 37, Plate XV.). Iron-ore formation, Inferior Oolite, near Blisworth :---

Specific gravity 3.58.

Protoxide of iron	49.58 = 79.9 carbonate of iron.
Sesquioxide of iron	5.67
Bisulphide of iron	0.96 = iron 0.45, sulphur 0.51 .
Protoxide of manganese	0.16
Alumina	1.56
Lime	3.24 = 5.8 carbonate of lime.
Magnesia	0.46 = 1.0 carbonate of magnesia.
Carbonic acid	34.64
Phosphoric acid	0.44
Silica	2.16
Organic matter	Trace.
Water of combination	1.56
1	100.43

Still lower down, near the base of the deposit, are some green patches, likewise environed by a sinuous line of the brown ferruginous cake. Except in colour, they resemble in aspect and texture the general

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earthy ground of the deposit, being made up of incoherent Oolitie grains. The following is their composition.

Analysis No. 77, by Mr. David Forbes, of green patches at base of Northamptonshire iron-ore deposit (fig. 37, Plate XV.).

Protoxide of iron	40.93
Sesquioxide of iron	6.14
Protoxide of manganese	0.16
Alumina	8.08
Lime	3.47
Magnesia	2.21
Potash	0.19
Soda	0.27
Sulphurtrace	
Carbonic acid	
Phosphoric acid	1.99
Silica	9.04
Water	4.92

99.72*

The specific gravity at 60° Fahr. was found to be 3.401; and an examination by the microscope showed it to consist almost entirely of two mineral constituents—the one crystalline and colourless, being chiefly carbonate of iron, and the other of a green colour, probably silicate of alumina and iron. Whether the green colour is due to it or to the presence of phosphate of iron is not decided, but it appears probable that a green silicate does exist in the mineral.

It may be roughly estimated to consist of

80 per cent. of carbonate of iron,

7 per cent. of carbonates of lime and magnesia,

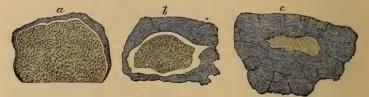
 $11\frac{1}{2}$ per cent. of silicates of iron and alumina with phosphoric acid, and $1\frac{1}{2}$ per cent. of water.

It will be seen, therefore, that the composition of the grey nodules, and likewise of the friable green patches, is essentially different from that of the mass of the deposit, and, furthermore, that their isolated disposition excludes the possibility of a separate mechanical origin. The question then arises, whether any of the states of combination in which the iron now occurs in the bed, was its primordial condition, and which of the other conditions have been subsequently induced. The nodules of subcrystalline carbonate of iron forming the upper grey course are clearly of secondary origin, and appear to have been segregated out of the general mass; and the lower green patches do not differ much from them in composition, though retaining the original colitic structure of the rock. Mr. Sorby (Proceedings of the Geological and Polytechnic Society of the West Riding of Yorkshire for 1856-57, p. 457) has shown that, in the Cleveland iron ore of the Lias Marlstone, carbonate of iron has become substituted for carbonate of lime in fossil shells and oolitic grains; and it appears probable that these similar masses in the Northampton-

* The composition closely resembles that of the Cleveland iron ore analyzed by Mr. Dick, and given at page 57 of the 12th volume of the Quarterly Journal of the Society. shire beds are due to segregation, in which carbonate of iron has in like manner been drawn towards centres of aggregation, whilst the hydrous sesquioxide has been dispersed, in the form of receding bands, out of an original matrix containing both the carbonate of protoxide, and sesquioxide of iron in association. The phosphoric acid appears to have been nearly all aggregated with the carbonate of iron, scarcely any occurring in the brown cakes of sesquioxide; and the carbonic acid has also been almost entirely withdrawn from the brown bands and general mass of stratum to the centres of aggregation of the protoxide of iron. It may here be noticed that concretions of carbonate of iron, wherever occurring, invariably present the uniformly homogeneous structure * observed in those of the Northamptonshire beds, whilst nodules of sesquioxide of iron are characterized by a concentric banding, such as would be the result of successive accumulations of the concentrating lines observed in yellow-banded sandstones (fig. 60, p. 393).

Kernel-roasting.—The artificial process known as "kernel-roasting" of copper ores presents some phenomena so closely resembling the mode of aggregation of the oxides of iron in yellow-banded sandstones, that a brief reference to it may not be inapplicable as illustrating the kind of motion which the iron appears to have taken. A full description will be found at p. 349 of 'Percy's Metallurgy,' from which the following is abridged. When cupriferous iron pyrites containing, say, from one to two per cent. of copper, in lumps about as large as the fist, is subject to a very gradual roasting at a low heat with access of air, it is found that a large portion of the copper becomes concentrated in the centre of each lump (fig. 63⁺).

Fig. 63 .--- " Kernel-roasting" of Copper Ores.



In the early part of the process, a lump broken across (a and b) consists of a central mass of unchanged ore, enclosed in a shell of a reddish-brown substance like sesquioxide of iron; and between the two is interposed a thin, more or less continuous layer containing more copper than the original ore. At about the middle of the roasting, several such concentric layers may be observed; and when the process is further advanced, a nucleus of unchanged ore can no longer be seen, the outer brown crust becomes greatly increased, and the concentric stratification of the copper layers is still visible.

* Merely as regards the absence of banding, as subsequent brecciation has frequently produced complex modifications in the original structure.

+ For the use of this engraving I am indebted to the kindness of Dr. Percy.

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DISPOSITION OF IRON IN VARIEGATED STRATA.



Anhydrous Sesquioxide of Iron.



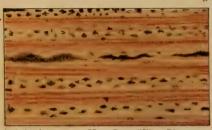
Hydrous Sesquioxide of



Carbonate of Protoxide of Iron.



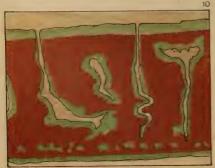
Gres bigarre, Trias, Baccarat, France.



5 Grès des Vosges, Near Raon l'Etape, Vosges



⁵ Permian, Kemberton Pits, near Madeley, Salop



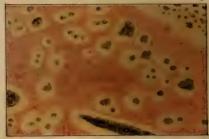
Keuper Sandstone & Marl Alderley Copper Mine Cheshire



Red Beds Nº Torquay, S. Devon .



Pebble Bed in Carboniferous Limestone, Trevor, nr Llangollen,



Permian Coalport, Shropshire.



Theuper Sandstone & Marl Alderley Copper Mine Cheshire.

DISPOSITION OF IRON IN VARIEGATED STRATA.

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Grès Bigarré, Trias, France, Stone De basement of Palace of Industry Paris .



Keuper Marls, Worcester Station.



Marnes irisées, Trias, Enville Lunéville, France



14

20 Old Red Sandstone, Kerriemuir Forfarshire.



Permian Marls, Railway Cutting. near Linley Shropshire.

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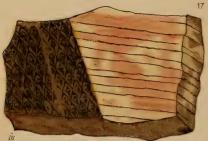


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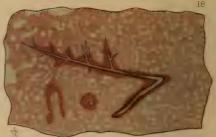


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Environs of Ardenay, Marne et Loire, Museum of Jardin des Plantes, Paris.



Terrain houller, Sarrebrick Museum of 20 Jardin des Plantes Paris. 21



5 Great Oolite, Kingsthorpe. Northampton.



*Marl under Glaises-Vertes, Butte-Chaumont Paris



³ Argile Plastique Vaugrard. Paris 2:



To Upper Purbek Marble, Woody-Hyde, Swanape



Lower Bagshot Clays . Nº Wareham .



* Cambrian, Bayston Hill, near Shrewsbury.



¹Surface Clay, Benthall, Shropshire.



Lower Green, Sand West of Folkstone,

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Carboniferous, Railway Cutling nr Bewelley, Worecstershire .



Caradoc Sandstone, Horderley.Salop.



Banded Cambrian States with intrusive dyke of Diabase, Carnarvonshire



Lower Silurian[®] Head of Crummuck Water, Austwick, near Clapham, Yoi kshire



· Cambrian Slate Penrhyn Quarries



12 Cambrian Slate. Glynn Quarries Lilnberis



DISPOSITION OF IRON IN VARIEGATED STRATA



Ashdown Sands. Wealden Hastings.



Horsham Stone Wealden



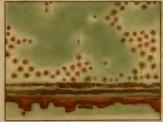
Calcaire Grossier Chaville Railway Station near Paris.



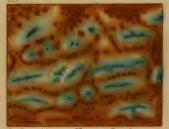
Keuper Sandstone.Clive Copper Mine . Shropshire.



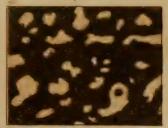
Iron Ore formation. Inferior Oolite



Cupriferous Keuper Sandstone. Alderley, Cheshire.



Cupriferous Keuper Sandstone. Alderley Cheshire.



Keuper Sandstone Clive Hill . Shropshire



In the last stage (c) the concentric arrangement disappears, and the great bulk of the copper is accumulated as a central nucleus in the condition of rich copper regulus. In large lumps several such nuclei may be formed.

The various chemical changes taking place in the several stages, which have been investigated by Lürzer, are fully described by Dr. Percy; but a satisfactory explanation of the *character of the* motion of the copper towards a central nucleus seems wanting. It cannot be the result of the mechanical aggregation of fused particles, as the heat is not carried nearly to the melting-point, or even to plastic fusion; indeed the action is arrested beyond a certain temperature, and concentration is not the only phenomenon.

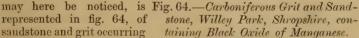
Mr. D. Forbes states that when silver is present in the ores, it appears to *travel outwards*, and that he has seen some specimens in which the outer surface of the piece of roasted ore was covered by a thin shell of metallic silver, as if electro-deposited. The phenomena, if not analogous, bear a curious resemblance to the kind of changes which have taken place in the Northamptonshire iron-ore beds, in which the protoxide of iron, and phosphoric and carbonic acids, have been aggregated towards definite centres, whilst the sesquioxide has been repelled from such centres in concentric ferruginous bands, travelling outwards until arrested by mutual contact.

I believe that many of the phenomena connected with banded agatescent and other concretions will be found analogous in character to these phenomena, and to the ferruginous banding of yellow strata—their accumulation having taken place in convergent or retrogressive lines within a solid matrix, producing a structure resembling the mechanical superposition of successive coats.

14. Disposition of Manganese in Variegated Strata.—Another case of secondary variegation, resembling, though independent of, the occurrence of iron, which

may here be noticed, is represented in fig. 64, of sandstone and grit occurring at the base of the Shropshire Coal-measures. The black fields of colour are due to sesquioxide of manganese: they vertically intersect successive beds of conglomerate and sandstone; and their disposition is obviously due to some cause independent of mechanical arrangement, analogous to the forces that have operated in the rearrangement of iron.

15. General conclusions.— In comparing the composi-





tion of the different coloured areas of variegated strata, one of the most VOL. XXIV.—PART I. 2 F PROCEEDINGS OF THE GEOLOGICAL SOCIETY. [April 22,

striking points is the very small proportion of the numerous forms of variegation that can be accounted for by the mere altered state of combination of the iron *in situ*.

The occasional conversion of the red anhydrous sesquioxide, or the lower hydrates, into fully hydrous sesquioxide, the reduction of sesquioxide to protoxide of iron in the production of green slates, and the exceptional cases of the alteration of colour of red beds by the decomposition of bisulphide of iron complete the list of colouralterations by simple chemical change.

Even the agency of organic matter in inducing chemical changes in the state of combination of the iron, will not in most cases account for the bleaching—the segregational motion of the colouring oxide, which is the ultimate cause of the variegation, being supplemental to the simple chemical changes of combination. The great majority of cases of variegation are independent of altered combinations, and more often than otherwise seem to have been induced by agencies not directly connected with chemical change. The transference of the colouring oxide from one part of the stratum to another has taken place by the simple mechanical agencies of infiltration and dissolution, as well as by segregation; but the latter, above all other agencies, has played the largest part in the variegation of ferruginous rocks.

2. On the Older Rocks of South Devon and East Cornwall*. By HARVEY B. Holl, M.D., F.G.S.

[Plate XVI.]

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I. INTRODUCTION.

In the course of last year I made an examination of the older rocks of South Devon and the adjacent portions of Cornwall, for the purpose of ascertaining the stratigraphical relations of the different beds, or groups of beds, with a view to their coordination with the more complete and better-known series in the northern part of the county. I was led to undertake this in the belief that, notwithstanding the many memoirs that have appeared on Devonian Geology, there was still a very great difference of opinion among geologists respecting

* This memoir is illustrated by an Ordnance Map coloured geologically, from which Pl. XVI. has been reduced.

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