ON THE GEOLOGICAL ACTION OF THE HUMUS ACIDS. By ALEXIS A. JULIEN, of New York, N. Y.

I. INTRODUCTION.

§ 1. *The Humus layer.*—Throughout all geological periods, whose records are within our observation, even the Archæan, a zone of gentle but ceaseless chemical action has enveloped the earth, whose efficiency in extensive subterranean alteration seems yet to be but partially recognized. Now, as in the past, it is represented by the thin sub-aërial layer of humus, which constitutes the soil of forests and savannas, and the muck of fresh and brackish-water swamps. Intervening between the crystalline mineral substances of unstable composition below and the layer of atmosphere above—a storehouse of gaseous and liquid agencies of decomposition and removal—this layer of humus has been the medium of continual reaction and change. Especially has it served as a laboratory for the production of a series of acids, which have been constantly transferred over the surface by streams and within the interior by percolating solutions, and as constantly renewed.

§ 2. *Efficiency of organic acids.*—A recently published investigation[1] by a Fellow of this Association has directed attention to a power of decomposition and corrosion, little suspected, of several common organic acids, both in artificial application and in the field of geological phenomena. From the data there given of the results of his examination of two hundred minerals, the brief tabular statement (page 312) presents the reactions nearly allied to those obtaining in nature: the minerals selected being those of most common occurrence in rocks and veins.

In regard to these two methods of treatment, negative results were obtained with a large number of minerals, *e. g.*, pyrite, chalcopyrite, augite, hornblende, the feldspars, micas, olivine, fluorite, etc.; but the nature and strength of the solvent employed, and the brief duration of each trial, seem at present insufficient to justify generalization, notwithstanding the suggestiveness of certain results.

My present purpose is to extend the series of illustrations of the character and extent of the geological phenomena, both from

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[1] "Application of Organic Acids to the Examination of Minerals," H. Carrington Bolton, Ann. N. Y. Acad. Sci., 1877-78, I, 1, 153.

recent personal observations and from published but hitherto disconnected facts. It will be understood that although little or no reference may be made to other solvents, such as water itself, various mineral acids, and saline solutions, their agency in nature

MINERALS DECOMPOSED (IN FINE POWDER) BY A SATURATED SOLUTION OF CITRIC ACID.

IN THE COLD.

A.	B.	C.	D.
Without evolution of Gas.	*With liberation of CO_2.*	*With liberation of H_2S.*	*With separation of SiO_2.*
Clausthalite, Leucopyrite, Brucite, Pyromorphite,* Vivianite. ! Wavellite, Anglesite. Brochantite. !	Calcite. ! Dolomite,* Gurhofite, ! Ankerite,* Rhodochrosite,* Smithsonite,* Aragonite, ! Witherite, ! Strontianite, ! Cerussite, ! Malachite, ! Azurite.*	Stibnite, Galenite, Sphalerite, Pyrrhotite.	Wollastonite, Rhodonite, ! Chrysolite, Willemite, !‡ Nephelite. Chondrodite, Pectolite. !‡ Laumontite, !‡ Chrysocolla, ! Calamine. !‡ Apophyllite, Thomsonite, ! Natrolite, !‡ Mesolite. ! Analcite, Chabazite, Stilbite. Deweylite, Prochlorite.

ON BOILING.

E.	F.	G.	H.
Without evolution of Gas.	*With liberation of CO_2.*	*With liberation of H_2S.*	*With separation of SiO_2.*
Cuprite, ! Zincite, Goethite.* Limonite,* Apatite.* Gypsum,*	Hausmannite,† Pyrolusite.† Manganite.† Psilomelane, !† Wad, !† Magnesite, ! Siderite, !	Bornite, Jamesonite,* Bournonite.* Boulangerite,	Tephroite,‡ Ilvaite. Phlogopite,* Datolite. !‡ Prehnite,* Heulandite, Serpentine, Bastite,
and those in A.	*and those in B.*	*and those in C.*	*and those in D.*

! Completely decomposed or dissolved. * Feebly attacked.

† The CO_2 evolved is derived from the Citric Acid. ‡ Gelatinizes.

is not ignored; nor is any attempt now made to compare their relative efficiency with that of the special agency under discussion. Neither is the important and broad subject of the geological work of "organic matter" included, with reference to its general reducing influence, the development of gases, the accumulation of carbon, etc.

II. MATERIALS YIELDING HUMUS ACIDS.

§ 3. *Varieties of humus.*—In nature, the complex mixture of organic substances, styled humus, is found under many forms: the *brown* variety, in living vegetation, in the outer bark of many trees, in the excrescences attending unhealthy growth, especially studied in those of the elm, and in the mould and ergot of many grains and grasses, in many fungi, etc., in the dead leaves hanging to trees, the upper and drier layers of the fallen litter and of peat, and the decaying sea-weeds upon the shores: the *black* variety, in a more or less active state of decomposition, in the deeper layers of the soil, of the rotting leaves and wood of the forest, and of the mud, muck, and peat of swamps, bogs, and ponds, in the dung of animals, birds, etc.: in a state of transference, in the waters of springs, mineral-waters, rivers, lakes, and even in rain-water: and in a fossil condition, not only in lignite, brown-coal, and many carbonaceous deposits, but locked up in the hygroscopic water and organic matter of many minerals and especially of many hydrated ores of iron and manganese.

§ 4. *Forest-litter.*—The chemical constitution of the forest-litter of fallen leaves, and of the humus produced by their decay, has been the subject of investigation by several analysts, for agricultural purposes; but these results are of little use for further application, on account both of their limited number and of the common neglect to estimate, in each locality, the influence of the character of the soil. Some of the observations of Krutzsch[2], Ebermayer[3], and Dulk are presented on page 314.

The variations in lime and silica in the above analyses are attributed chiefly to the soil. It is found that the presence of tannin or resinous matter retards decomposition, while that of the alkalies and lime assist it. In Bavarian forests, with the coniferous trees, a period of from three to eight years is necessary for

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[2] Chem. Ackersmann, 1866, 158. [3] Landw. Vers. Stat., 1875, XVIII, 62–77, 205.

the formation of humus from the leaf-litter, but with deciduous trees from two to five years are sufficient.[4]

FOREST LITTER.	*Nitrogen.*	K^2O	Na^2O	CaO	MgO	Fe^2O^3	P^2O^5	SO^3	SiO^2	Total ash
Beech	0.8 to 1.24	2.81	.56	24.49	3.50	1.73	2.98	1.10	18.37	55.9
Oak	1.05	3.28	1.28	22.68	3.80	1.03	2.95	1.51	18.83	55.1
Spruce fir	1.35	1.61	.56	20.27	2.32	.93	2.14	.70	16.54	45.3
Scotch pine	1.89	1.51	.61	5.82	1.51	.49	1.11	.57	2.12	14.7
HUMUS.										
Beech forest		1.53	.26	10.22	2.54	3.97	2.79	1.86	20.03	43.2
Fir forest		2.19	.39	23.39	1.79	2.50	4.19	1.76	7.80	44.

§ 5. *Composition of humus.*—The nature of the decomposition which thus takes place is partially represented by the following ultimate analyses[5] of the peat at different depths in a peat-bog of the Nienwalder High-moor of Gutes Jessback, in Holstein.

	Ash	N	C	H	O
Brown peat from the surface,	2.72	.80	57.75	5.43	36.02
Nearly black peat, at a depth of 7 feet,	7.42	2.10	62.02	5.21	30.67
Black peat, at a depth of 14 feet,	9.16	4.05	64.07	5.01	26.87

The above results indicate a gradual downward transference and concentration near the bottom of the bog, both of the more carbonaceous and nitrogenous matters of humus, by loss of water and oxygen, and of most constituents of the mineral matter. The character of the latter is shown in several good analyses of peat and muck (Johnson's Essays on Manures. Cook, Rep. Geol. N. J., 1863, 481, and 1878, 47); but exact determinations of the carbonaceous matters are very rare. A peat from the vicinity of Moscow, Russia, gave Hermann[6] the following percentages: Muck-carbon, nitrolin, and plant-remains, 77.5: humic acid, 17.: humus extract, 4.: ammonia, 0.25: crenic acids, traces: ash, 1.25; in another peat, muck-carbon, etc., 80.: apocrenic acids, 17.: crenic acids, 1.: ash 2. The virgin-soil of the "black earth" (Tschornozem) of the Russian steppes[7] yielded the following per-

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[4] Ebermayer, Gesammte Lehre der Waldstein: See Watts Dict., III Suppl., Part I, 823.

[5] Detmer, Landw. Vers. Stat., 1871, 270.

[6] R. Hermann, Erd. Jour. f. pr. Ch., 1842, XXVII, 165.

[7] R. Hermann, *idem*, 1837, XII, 290, and 1842, XXVII, 174.

centages; sand, clay, etc., 89.58: nitrolin, etc., 1.66: humic acid, 1.77: humus extract, 3.10: torfic acid, 1.77: crenic acids, 2.12.

The inorganic matters in peat-moss (Sphagnum), as represented by its ash, amount to 3 to 4 per cent., and in dried peat from about 1 to 25 per cent., averaging in the denser varieties 15 per cent. In the careful investigation by Vohl[8] of the peat of a high moor in the Canton Zürich, containing 0.92 per cent. of ash, he obtained the following results, briefly summarized. The large content of alkalies (20 per cent. of the ash) and of silica (42 per cent.), in the moss, have been mainly carried off into the bog-waters, only 3 or 4 per cent. of each remaining in the peat; the same substances are also drawn up by the later vegetation, and thus occurs upwardly "a transference of these mineral substances from one peat layer to another." Of the remaining constituents, present in small quantity in the moss, there has been a heavy concentration of alumina, ferric oxide, and lime in the peat, and even of phosphoric and sulphuric acids in a less degree.

Many instances have been noted of the occurrence in peat bogs, etc., of layers of pulverulent calcium carbonate, resulting probably from the decomposition of ammonia-lime double salts of the humus acids.[9]

Peat sometimes abounds in pyrite, and the decomposition of this mineral contributes a basic ferric sulphate to the bog ores afterwards produced.[10]

§ 6. *Nitrogen in humus.*—Natural humus (*e. g.*, from peat) is found to contain from 1 to 3 per cent., or more, of nitrogen, and the dry soil of forests from 0.00012 to 0.00087 per cent. of ammonia. The nitrogen-content in peat, which has a very important office, has been attributed to the decomposition of the albuminoid substances of living vegetation, to direct absorption of nitrogen gas from the air by humus, during its oxidation,[11] and of nitric and nitrous acids and ammonia from atmospheric waters,[12] etc. Schultzenstein attributes it to the infusoria, polyps, worms, mollusks, crustaceans, and insects, which live in the peat and soil; but these very animals must have derived their nitrogen from the living plants and humus-remains on which they feed. As

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[8] Ann. Ch. Pharm., 1859, CIX, 185.

[9] Roth, Allg. u. Ch. Geol., 1879, I, 596.

[10] Roth, *idem*, 598–9.

[11] P. P. Dehérain, Compt. rend., 1872, LXXIII, 1352.

[12] P. Bretschneider, Chem. Ackersm., 1871, 187.

Dr. J. H. Gilbert has shown,[13] the evidence in regard to the *source* of the nitrogen is still contradictory and the question must be considered unsettled. But in regard to its *accumulation*, in a form having little tendency to decomposition, an important condition is shown in the enclosure of animal remains, especially the exuviæ of insects, of which certain species swarm in vast numbers under the shelter of swamp vegetation. A recent observer in the western territories reports the superficial layer of a peat-bog to contain a remarkable abundance of the wing-cases of beetles. Prof. S. H. Scudder of Cambridge, Mass., has recently reported a similar occurrence of insect-remains in a partially submerged bed of peat at Nantucket; and one incidental result of the investigations by himself and others, on the insect-fauna of the Carboniferous strata and of carbonaceous shales of other periods, is the increasing evidence of an abundance of insect-life in those ancient marshes, proportionate to the richness of vegetation and depth of marsh-deposits, indicated by the present accumulation of fossil carbon. These facts, and those known in regard to the character of the fauna of the swamps and bogs of the present day, seem to indicate at least that the concentration of nitrogen in a comparatively stable form, yielding a steady supply of that element for the formation of the azotized combinations of the humic acids, has been largely dependent upon the accumulation of the exuviæ of insects within the humus deposits.

Its concentration in the lower layers, noted by Detmer and explained (*loc. cit.*) by the supposition that "the nitrogenous, perhaps leather-like bodies, which are formed, are decomposable with very great difficulty," may be simply due to the survival of such exuviæ in the form of chitin. It has also been suggested that the oolitic structure, in a Belgian iron-stone of Devonian age, has been due to the eggs of aquatic insects which the iron-ochre has incrusted, like the same structure in the recent oolitic limestone of the great lakes of Mexico.[14]

The important chemical agencies and results, afterwards described, appear therefore to depend for their genesis, at least largely, upon this relationship to the insect-world: *e. g.*, the iron-ores of the Archæan strata, the extensive iron-stone layers associated with the coal, and the profound chemical erosion, which

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[13] Am. J. Sci., 1877, (3), XIII, 20, 99, 181.

[14] T. L. Phipson, Compt. rend., 1861, LII, 975.

preceded and rendered possible the enormous denudation of northern areas during the Glacial period.

§ 7. *Distribution of humus.*—A brief reference may also be made to the geographical distribution of the humus-layer. On land, even in its thinnest development, as under cryptogamous growth upon rocks, it seems endued with special activity for corrosion. In ordinary soils its wide extension is well known, but there are special varieties which seem to be exceptionally rich, *e. g.*, the "Regur" or rich cotton-soil of Hindostan,[15] the productive thick humus of the American prairies and of the Southern steppes of Wallachia, Moldavia, etc., especially the "Tchornozem" or "black earth" of the steppes of southern Russia.[16] The latter occupies the centre of a trough 200 millions of acres in extent. It contains 6 to 10 per cent. of organic matter, consisting of humic, crenic, apocrenic acids, etc., and 2.45 per cent. of nitrogen, by the analysis of Payen. In the depressions of the surface, near the water-courses, lakes, and seas, occur still richer accumulations of humus in the form of peat-bogs, swamps, and salt-marshes, which even girdle the continents; and there are many reasons to believe that the very bed of the ocean, in its profoundest depths, supports deposits in which humus-like products of decomposition play their part.

An attempt has been made in the Plate to give a general view of the superficial extent of chemical corrosion and decomposition now in progress by these agencies throughout the world. The dark areas represent, with some exaggeration of effect, the richest deposits of humus, in which the chemical action is presumably most active, *e. g.*, rich soils, layers of humus upon the flanks of mountain ranges, fresh-water swamps near lakes and along the courses of rivers, and salt-marshes along oceanic shores. The lighter shading represents the inferior degree of chemical action exerted by ordinary soils, rock-surfaces covered with cryptogameæ, etc. The areas free from shading are those in which there is little vegetable growth except during short seasons of heavy rains or summer warmth, *e. g.*, arid deserts, the summits of high mountains, tracts of sandy dunes, and the ice-capped Arctic and Antarctic regions. The *Tundra* belt, along the northern border of

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[15] Capt. Newbold, Rec. of Roy. Soc.

[16] R. I. Murchison, Russia and the Ural Mts., Geol., 1845, I, 557 *et seq.*, and Trans. Roy Agric. Soc., III, 1; also F. Schmidt, Zeits. d. D. geol. Gesells., 1877, XXIX, 830, 835; and R. Hermann, *loc. cit.*

the continents, is an area made up of frozen mossy swamps and rocky hummocks covered with lichens, mosses, and saxifrages; it must comprise a considerable amount of humus of an acid character. A comparison of this map with the published geological charts, which show the regions covered by coal-basins, affords some conclusions of interest, especially confirming the shifting position of the areas of extreme erosion at different periods.

III. ACIDS EXISTING IN HUMUS.

The organic acids, resulting from the decomposition of humus, appear to be numerous and very unstable; their investigation has as yet been only begun, and even the results so far attained are vitiated, for our present purpose, by the general absence of discrimination between the characteristics and reactions existing in nature, and those produced by the artificial conditions of laboratory investigation. Having eliminated, therefore, all observations which appear to be exclusively artificial, and all which have no apparent geological bearing, I will now briefly describe the particular acids which probably are actually diffused through humus and its natural solutions. Of course but very few of these acids are actually present in most deposits of humus; the larger number are evanescent in their duration, but *contribute* to the acid character of the organic salts in all natural humus.

§ 8. *Inert substances.*—Two constituents of humus exist and may first be mentioned, which are insoluble in water, acids, and alkalies, which are amorphous, neutral, inert, and yet serve, by oxidation of their abundant material, to furnish a continual supply of the soluble acids, and, by their absorptive powers, a supply of nitrogen to form their nitrogenous combinations and ammoniacal salts. *Nitrolin*, the principal constituent of rotten wood, is of a brown color, containing 56.13 per cent. of carbon and 4.00 to 12.30 per cent. of nitrogen. *Humin*, the principal constituent of the true humus, is of a black color, but is too closely intermixed with woody-fibre and nitrolin to permit its accurate analysis. Hermann also finds *anitrohumin* in peat. Mulder studied humin (and humic acid) as obtained from the *black* compact peat of the Haarlem sea; but he also distinguished *ulmine* (and ulmic acid), as occurring in rotten wood and in the *light-brown* Frisian peat. To the latter he assigns the formula, $C^{20} H^{16} 0^{7}$ (or, $C^{12} H^{9.6} O^{4.2}$, as H. Wurtz[17] suggests, making it isologous with cellulose, $C^{12} H^{20} O^{10}$) ; but it is probably a mixture of two or more compounds. He obtained a substance, termed humus or humine ($C^{12} H^{9} O^{4.5}$, Wurtz), as the product of oxidation of ulmine, with separation of water; and he suggested that this action is in constant progress in the mud upon the bottom of lakes, etc.

A collation of the most reliable investigations yet made has furnished the following summary of the chief organic acids in humus.

§ 9. *Humic Acid.*—This is found in decayed wood, especially that of the elm and beech, and in peat, vegetable mould, etc. A large proportion (ulmic acid?) is said to occur in the prairie soil of this country.[18]

Percentage Composition.

	C	H	O
Humic Acid (with 3 aq.)	64.	4.	32.
" " from peat (Detmer[19])	59.74	4.48	35.78
" " " soil (Bretschneider[20])	60.39	4.50	35.03
Ulmic Acid from brown peat (Mulder[21])	62.62	4.62	32.76
" " (with 1 aq.)	67.1	4.2	28.7

Stein concludes that the ulmic acid and ulmine of Mulder are isomeric, with the formula $C^{24} H^{18} O^{9}$, and Detmer considers the ulmic acid identical with humic acid and produced by drying at too high a temperature. The generally accepted results of the more recent analysts, such as Detmer and Bretschneider, render it probable that nitrogen is unessential to the constitution of this acid, and the analyses containing it are therefore excluded. The formulas ascribed to the acid are as follows:

		(H. WURTZ.)
Humic Acid (Detmer)	$C^{60} H^{54} O^{27}$	
" " (Mulder)	$C^{20} H^{12} O^{6}$	
Geic " (")	$C^{20} H^{12} O^{7}$	$C^{12} H^{7.2} O^{4.2}$
Ulmic " (")	$C^{20} H^{14} O^{6}$	$C^{12} H^{7.4} O^{3.6}$
		or perhaps $C^{24} H^{18} O^{8}$

Humic acid possesses a strictly colloid nature, and, as found

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[17] Johnson's Cyclopedia, article "Humus."

[18] L. Lesquereux, Geol. of Ill., 1866, I, 252.

[19] Landw. Vers. Stat., 1871, XIV, 260.

[20] Chem. Ackers., 1871, 287.

[21] Bull. de Sci. phys. et nat. de Neerl., 1840, 1—102: abstract in Ann. der Chem., 1840, XXXVI, 243.

by the direct experiments of Detmer,[22] is not absorbed by the rootlets of plants, though its oxidation-products (*e.g.*, crenic acid) appear to be taken up.

While moist it is black, has an acid taste and reddens blue litmus-paper, absorbs oxygen and yields carbon dioxide by natural decomposition ; it dissolves in 8333 parts of water at 6°C., and in 625 parts at 100°C. Its solubility is diminished by the presence of salts, and it is insoluble in water free from nitrogen or air.[23] After drying at 120°C., it dissolves in 13784 parts of water at 15°C., and, after perfect drying, at high temperatures, becomes insoluble.

It is far more soluble in aqueous solutions of the alkalies. It expels carbon dioxide from metallic carbonates, but can also be expelled by that acid from all combinations. All its salts are black. Its alkaline salts are easily soluble, but those of the alkaline earths and metallic oxides are not soluble or only with very great difficulty. Yet its insoluble salts are soluble in aqueous alkalies, especially in ammonia and its carbonate, and partly also in aqueous alkaline carbonates. Humic acid does not combine with silica, unless ammonia be present.

It has also the colloidal property of gluing together vegetable earths, such as the siliceous sands of the Landes near Bordeaux, into a layer impervious to water (called "alios")[24]; this has also been proved by direct experiment.[25]

Ammonium humate ($C^{60} H^{48} (NH^4)^6 O^{27}$, Detmer) dissolves in 22 parts of water, and exists in peat. According to Mulder, the formulas are as follows:

Humate, $C^{20} H^{12} O^6, NH^3, + 4$ or 5 aq., containing 60.1 per ct. C.
Ulmate, $C^{20} H^{14} O^6, NH^3 + 3$ aq., containing 61.2 per ct. C.

Sodium and potassium humates are soluble, as well as their double salts with ammonia.

Calcium humate dissolves in 3125 parts of water, and there is also a soluble double salt with ammonia ($C^{90} H^{46} Ca^3 (NH^4)^2 O^{27}$).

Magnesium humate dissolves pretty easily in water.

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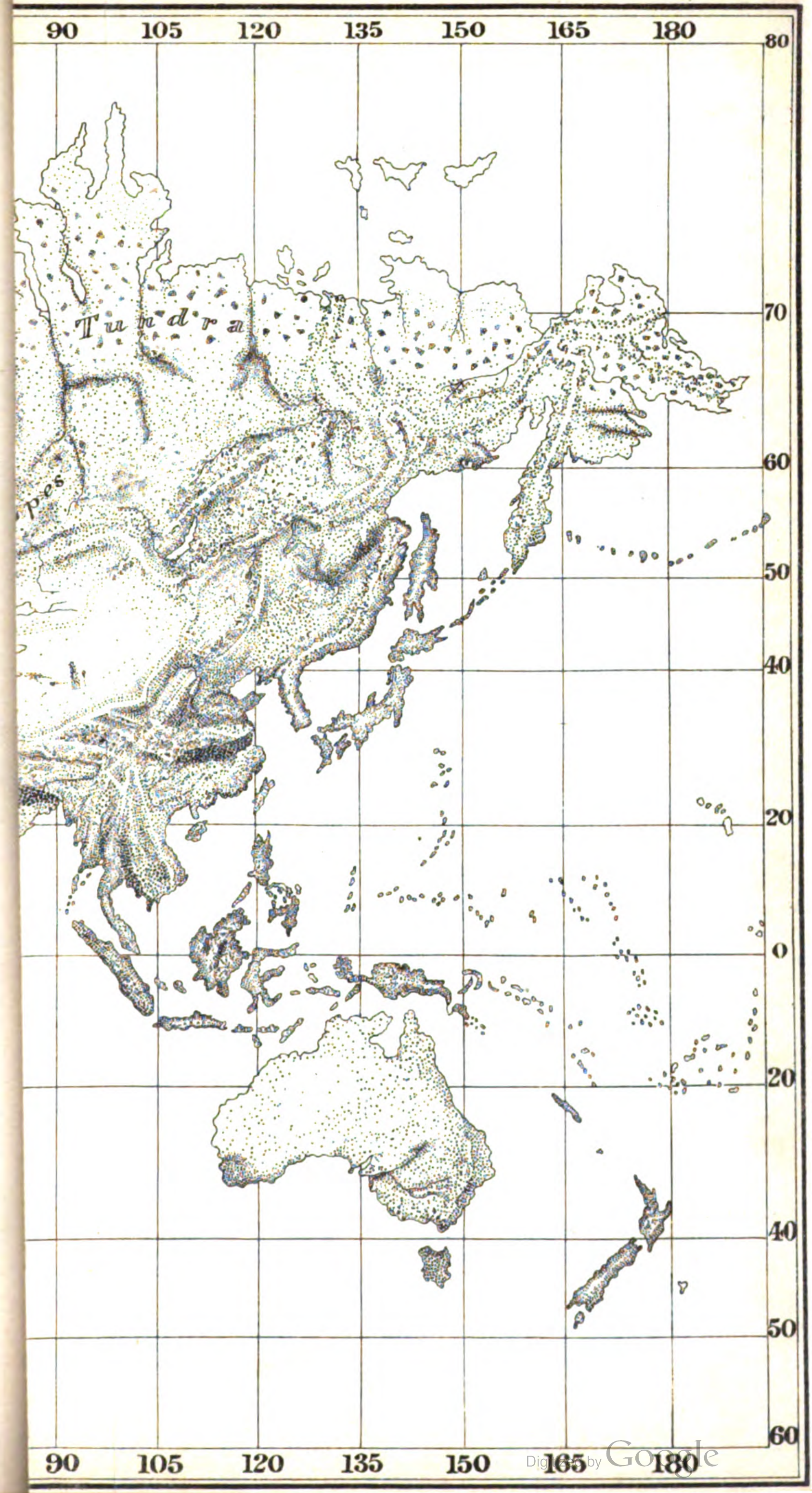
[22] Landw. Vers. Stat., 1872, XV, 284–286.
[23] E. Simon, Landw. Vers. Stat., 1875, XVIII, 452–472.
[24] Fauré, Ann. de Ch. et Phys., 1853, (3), XXXIX, 85.
[25] Th. Schloesing, Ann. de Ch. et Phys., 1874, (5), II, 532.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Ferric humate dissolves in 5000 parts of water at 19° C. (in 2300 parts according to Bischof),[26] and its double salt with ammonia ($C^{60} H^{46} (Fe^2)^{VI} (NH^4)^2 O^{27}$) is also soluble.

Manganic humate also forms a soluble double salt with ammonia.

An observation of great importance is that all humous acids absorb nitrogen from the air,[27] and that humic acid, mixed with solution of potassa, absorbs from the air 7.2 per cent. of nitrogen, and converts it into ammonia during oxidation; also the humus from old wood, mixed with solution of potassa, absorbs 3.6 per cent. of nitrogen.[28] On this ground the theory has been advanced that humic acid acts as the ammonia-provider in soils. Nitric acid is found to convert both ulmic and humic acids into formic and oxalic acids associated with ammonium-apocrenate.

Mulder finds that ulmic and humic acids "do not exist to much extent in the free state, except in bogs and morasses." In the soil they assume acid characters only by reaction with carbonates, and then become salts, *i. e.*, enter into combination. Other similar constituents of humus, soluble in water, of less certain character and determined composition, are the following:

Humous extract ($C^{16} H^{32} O^7 N^2$ (?), Hermann) occurs in tilled soil, peat, and rotten wood. It is brown and easily soluble in water, forms a sparingly soluble compound with lime, but presents mostly neutral properties.

Mudesous acid ($C^{12} H^{10} O^8$),[29] obtained, in combination with alumina, from pigotite, and probably derived from the decomposition of humus on moorlands.

Humous acid, obtained from Russian "black earth."

Azulmic acid[30] ($C^4 H^4 N^4 O^2$)[31] and *fumic acid*[32] obtained from rotten dung: the latter however, according to Mulder, being impure ammonium-humate.

Carbo-ulmic acid ($C^{40} H^{36} O^{16}$) and *Carbo-humic acid*, obtained from lignite.[33] These have yielded the following percentage composition:

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[26] G. Bischof, Chem. and Phys. Geol., I, 166.
[27] R. Hermann, Erd. Jour. f. pr. Ch., 1841, XXII, 69.
[28] Déhérain, Compt. rend., 1873, LXXIII, 1352.
[29] J. F. W. Johnston, Phil. Mag., 1840, XVII, 382.
[30] Braconnot, N. Ann. Ch. Phys., 12, 212.
[31] Pelouze and Richardson, Ann. Ch. Pharm., 1838, XXVI, 63.
[32] P. Thenard, Compt. rend., 1859, XLIX, 289.
[33] Herz, N. Repert, 10, 496.

	C	H	O
Carbo-ulmic acid	62.36	4.79	32.87
Carbo-humic acid	64.59	5.15	30.26

Ligno-humic acid ($C^{30} H^{60} O^{12} N^{6}$, Hermann), obtained from brown rotten wood, is somewhat soluble in water to a yellow solution, but is precipitated by mineral acids.

Anitro-humic acid ($C^{20} H^{40} O^{10}$, Hermann), obtained from peat, etc.

We have next to consider the products of higher oxidation of the feebly soluble acids thus far described. The most important are two, crenic and apocrenic, first identified by Berzelius, whose far greater solubility has resulted in their extensive distribution: so that they have been artificially separated for investigation, not only from peat and soils, but also from their widely diffused solutions in combination with iron and other bases.[34]

I have separated both these acids, in considerable quantity, from the peat which occurs at the southern end of Ballston Lake, in Saratoga County, N. Y.

§ 10. *Crenic acid.*—($C^{24} H^{24} O^{16} + 3 H^{2} O$, or $C^{24} H^{30} O^{19}$, Wurtz.) [Quellsaüre, Humusquellsaüre, Krensaüre, Brunnensaüre, etc.]

This occurs in the waters of probably all springs, rivers, lakes, etc., and in rain-water:[35] in rotten wood, peat, and tilled soil: and in bog ore, ochre, etc. It is of a pale yellow color and transparent, becoming yellow and opaque on drying; turns dark by exposure to the air, absorbs oxygen, and leaves a brown residue of apocrenic acid; is easily soluble in water, tastes sharply acid, reddens litmus, is styptic in strong solution, and forms white or light-colored neutral and acid salts. Salts of the alkalies are easily soluble, but less so than the pure acid, and are generally diffused; ammonium-crenate has been found in some iron ores.

Calcium-crenate is a neutral pale yellow salt, soluble in much water; a basic salt also exists, containing 20.59 per cent. of lime. Magnesium-crenate is easily soluble. Aluminum-crenate is a yellow salt, insoluble in water; with a larger proportion of acid, a soluble salt is formed, which, on addition of ammonia, is not precipitated but remains soluble. Ferrous crenate is soluble in acids; also in water, to a limpid and styptic solution, yielding

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[34] Gmelin's Handbook of Chem., XVII, 466—475.

[35] Salm Horstmar, Pogg. Ann., 1841, LIV, 254.

the usual reactions of a ferrous salt; but absorbs oxygen with extreme avidity, both from the air and from solid bodies, thus acting as a strong reducing agent, and passes into ferric crenate.

Ferric crenate is an earthy salt of a dirty-white color, or an ochreous brown flocculent deposit, insoluble in water (moderately soluble, according to Mulder and Bischof) and in acids. It dissolves completely in ammonia, so that, as Bischof remarks,[36] if there are decaying nitrogenous substances present, which evolve ammonia, *this salt may also be dissolved.* This apparently forgotten observation of Bischof may be of much geological importance, since it shows, contrary to the usual statements (LeConte,[37] Hunt,[38] etc.) that ferric crenate (and probably humate and apocrenate) *can* be dissolved, even without reduction, in ammoniacal solutions. On evaporation of the latter, they leave a reddish-yellow residue: from this residue water separates a soluble neutral double salt, leaving behind an insoluble basic salt. Manganese-crenate is moderately soluble (Mulder). Aluminum-crenate is insoluble (Mulder). The insoluble salts of both crenic and apocrenic acids are decomposed by and soluble in excess of solution of the alkaline salts. Silicic acid, precipitated from a liquid containing crenic acid, takes up a portion of the latter.

Hermann finds two groups of acids, the *crenic* and *oxycrenic* acids, occurring in nature, viz:

Humo-crenic acid ($C^{18} H^{36} O^9 N^4$), found in the "black earth:"

Torfo-crenic acid ($C^{15} H^{48} O^{12} N^4$), found in peat, "black earth," and mineral-waters:

Torf-oxycrenic acid ($C^{12} H^{12} O^4 N^4$), found in a mineral-water.

§ 11. *Apocrenic acid.*—($C^{24} H^{12} O^{12} + H^2 O$, or $C^{24} H^{14} O^{13}$, H. Wurtz.) (Quellsatzsaüre.) This occurs in the water of springs and rivers, in tilled soil, peat, decaying wood, and bog-ores. It is of a black-brown color, reddens litmus, has a styptic taste, and dissolves with brown color in water: some modifications are sparingly soluble. Crenic and apocrenic acids may be precipitated together by a mineral acid, out of an alkaline solution, as an amorphous light-brown mixture, very hygroscopic, with an acid reaction sufficiently strong to dissolve in the cold recently precipitated ferrous carbonate.[39]

The salts of this acid are amorphous, black-brown, easily

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[36] Op. cit., I, 166. [37] El. of Geol., 1879, 136. [38] Essays, 227.

[39] C. Boutigny, Compt. rend., 1871, LXXIII, 247.

soluble in water but generally less so than the crenates, both being generally more soluble than the corresponding humates. Ammonium-apocrenate is freely soluble in water, with an acid reaction. Potassium and sodium-apocrenates are black, neutral, and freely soluble in water, with brown color. Calcium-apocrenate is black-brown, gradually dissolves in water: there is also a basic salt, insoluble in water. Magnesium-apocrenate resembles that of lime. Two aluminum-apocrenates probably exist, in which the proportion of alumina is small; the one is a soluble salt, and the other, according to Mulder, insoluble. Neutral ferrous apocrenate is soluble, and is converted into basic ferric salt by exposure to the air. Basic ferrous apocrenate is black, insoluble, turning brown in the air. Neutral ferric apocrenate is soluble, and the basic salt insoluble. Manganese-apocrenate is moderately soluble. In regard to these two acids, Mulder observes (*op. cit.*, p. 350) that they exist in the soil nearly always as double salts of lime, iron, etc., with ammonia: that in the loose dry earth, apocrenic acid is formed by oxidation, and, in every soil, after rain, crenic acid by reduction, "so that the action or effects of these substances are alternately manifested."

Hermann divides his group of *apocrenic acids*, as follows: *Torfic acid* ($C^{20} H^{32} O^6 N^4$), found in peat, soil, and brown coal. Its alkaline salts are soluble, dark-brown, and absorb oxygen; its other salts are mostly insoluble in water.

Arvic acid ($C^{30} H^{48} O^6 N^{12}$), extracted from tilled soil.

Porla-apocrenic, from the Porla-water.

Anitro-apocrenic acid ($C^{20} H^{32} O^8$), obtained from peat.

§ 12. *Silico-azo-humic acids.*—The essential combination of silica with certain black acids of the soil was long ago remarked by Verdeil and Rislher; and A. Vogel has pointed out that "the assimilation of silica by a plant depends greatly on the amount of humus present in the soil." The existence of four azo-humic acids has been claimed by P. Thenard.[40] He believes that acids of this series "form spontaneously in the soil, at the expense of the humic acid, the ammonia of rain-water, nitrogen of the air, and of the silica preëxisting in the soil." He discovers that these acids dissolve silica in proportion to the nitrogen they contain, *i. e.*, from 7.5 to 24 per cent.; while with simple humic acids only 0.8 per cent. of silica could be experimentally dissolved, and

[40] Compt. rend., 1870, LXX, 1412.

even in these cases there was doubt of their purity. He further suspects that these organo-silicated combinations may pass into the organic combinations of Friedel,[41] silico-propionic acid, etc., in which silicon plays the part of carbon. Vogel finds that Thenard's compounds are soluble in very dilute alkalies, from which solution they can be separated unchanged.[42]

The solvency of silica in ammonium-crenate, and also in two weak acids, acetic and carbonic, has been shown (C. J. B. Karsten, Pogg. Ann. d. Ph. u. d. Ch., 1826, VI, 359), and the efficiency of others in the same direction does not therefore appear anomalous. It might be anticipated from the existence of a group of such powerful solvents of silica, occurring in great abundance and general distribution in nature, and freely soluble in atmospheric waters, that they must have exerted a decided influence in the decomposition and alteration of porous strata, especially above the water-level; and, in proof of this action, many instances will be given beyond. While the exact character of these acids has not yet (Mar., 1880) been reported, I shall not hesitate to use the name "silico-azohumic acids," merely, for the present, as a convenient term to distinguish the strong organic solvents of silica which undoubtedly exist in layers of humus.

§ 13. *Acids derived from vegetation, etc.*—In addition to the agency of these products of eremacausis, there is evidence, as Bolton suggests, of the "silent work of a higher class of organic acids" going on in the humus deposits. *Oxalic*, *malic*, *fumaric*, and an enormous number of acids, and their acid-salts with the alkaline metals and earths, are contributed, at least temporarily, by the leaves, stems, etc., of most plants, many of which are rich in raphides made up of minute crystals of those acids or their salts. The bark and excrescences of many shrubs and trees contribute *tannic* and *gallic* acids to the soil. "Falling fruits give it *citric*, *malic*, and *tartaric* acids," which however, in contact with decaying albuminoids, are partially converted into acetic acid, and rapidly and entirely into carbon dioxide.[43] Young roots, especially the finest fibrils, of living plants, contain an acid or acid-salt, which manifests a strong acid reaction to litmus paper.[44] The ground-

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[41] Bull. Soc. Chim., 1863, V, 174, 238; Compt. rend., 1870, LXX, 1407.

[42] N. Repert. Pharm., 1871, XX, 143–146.

[43] S. W. Johnson, How Crops Feed, 222.

[44] Zöller, Vs. St., 1862, V, 45.

pine (*Lycopodium complanatum*) contains malic acid, and its ashes 38 per cent. of alumina;[45] its rootlets also exhibit an acid reaction, probably due, in part at least, to the presence of acid aluminum-malate.[46]

"*Formic*, *propionic*, *acetic* and *butyric acids*, or rather their salts, have been detected, by Jongbloed and others, in garden-earth. The latter are common products of fermentation, a process that goes on in the juices of plants that have become a part of the soil."[47] The acids produced by the fermentation of bodies of the cellulose group are *lactic*, *butyric* and *acetic*, and these may possibly be sometimes present.[48] All these acids can scarcely exist, except temporarily and in very minute quantities, in the soil.

Uric acid ($C^5 H^4 N^4 O^3$), *Hippuric acid* ($C^9 H^9 N O^6$), and salts of acids of still more complex character are continually added by the dung of animals, birds, reptiles, and annelids. Recent observers[49] have called attention to the important office of the casts of the ordinary earth-worm (*Lumbricus terrestris*) in the soil layer, and also of the work of ants in covering rocks and in the alteration of soils. If salts of uric and formic acids have not been introduced by these means, at least a strong influence for the aeration and oxidation of humus has been exerted by these agents.

In the lichens the common acids are *oxalic* and *usnic*, but a long series of others have been detected. *Fumaric* and *lichenstearic acids* are present in many agarics; and *polyporic acid*[50] occurs in fungi upon decaying oaks, and, although itself insoluble in water, is found to unite with ammonia and the fixed alkalies in salts which are easily soluble. It has been pointed out that "the decay of forest litter is to a great extent brought about by the agency of fungi;"[51] and it may be inferred that even the more minute species both of fungi and lichens contain, or contribute during their

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[45] Salm Horstmar, Jour. f. Prakt. Chem., 1847, XL, 304.

[46] Ritthausen, *idem*, 1851, LIII, 420.

[47] Johnson, *op. cit.*, 222.

[48] Einhof. and v. Pontin; also R. Hermann, Erd. Jour. f. pr. Ch., 1837, XL, 280–281.

[49] White, Nat. Hist. of Selbourne, I. 14, 279; Knapp, Jour. of a Nat., 4th ed., 343; C. Darwin, "on formation of mould," Trans. Geol. Soc., 1840, (2), V, 505, *et seq.*; G. H. Kinahan, Geol. Mag., 1869, VI, 114, 263, 348; Prof. Paley, Hardw. Sci. Goss., 1878, XIV, 121, 154; M. Hensen, Nature, 1877, XVII (Zeits. f. wiss. Zool.).

[50] C. Stahlschmidt, Lieb. Ann. d. Ch., 1878, CLXXXVII, 177.

[51] Watt's Dict., III, Suppl., 823.

decay, supplies of additional organic acids, to be diffused, at least temporarily, through the humus. Overripe fruits are at once attacked, even upon the trees, by lichens and fungi, and, after they are fallen, become thoroughly permeated by these organisms and centres for their dissemination.

Mellitic acid ($C^{12} H^6 O^{12}$), found in the mellite of lignite-beds, and *succinic acid* ($C^4 H^6 O^4$), which is found ready formed in amber, etc., and is even yielded by the natural fermentation of malic, fumaric, and other acids, may here be mentioned. There is also a group of acid hydro-carbons, of uncertain character and composition, which have been detected by Williamson, Brückner, etc., in peat-bogs and brown-coal, viz., *georetic*, *geoceric*, *retinic*, *georetinic*, and *butyro-limnodic* acids.[52]

§ 14. *Acids from the atmosphere.*—It is certain also that the ceaseless and varied chemical reactions, which prevail among the constituents of the atmosphere, must yield continual contributions to the humus-layer, not only of carbon dioxide, but also of peroxide of hydrogen, of ozonized aqueous solutions,[53] and frequent supplies of other acids.

Nitric and *nitrous acids*, which meteoric waters contain, must be added in appreciable amount, chiefly in combination with ammonia, especially during summer-storms.[54] Nitrites are found in all arable soils,[55] being especially stored up in clays: Chabrier estimates that a hectare of arable ground, to the depth of 30 cm., receives annually 3.75 kgms. of nitrous acid.[56] The existence and permanence of these acids in deposits rich in humus must probably be ephemeral; in fact nitrous acid is found by Chabrier to pass rapidly into nitric acid, while Kuhlman believes that they are both reduced almost instantaneously to ammonia. Nevertheless, even their temporary action may be of some moment in this connection, as tending to the conversion of humus into ammonium-apocrenate and organic acids of the higher oxidation: such as formic and oxalic acids, as found by laboratory experiment. *Hydrochloric acid*[57] is also found diffused, in minute quantity, in the air above salt marshes.

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[52] Gmelin's Handbook, XVII, 444, etc. Dana, Syst. of Min., 747, etc.

[53] R. Leeds, Ann. N. Y. Acad. Sci., 1879, I; D. ch. Gesells., 1879, XII, 183.

[54] Sometimes producing an acid rain, Ducrès, Jour. de Pharm., 1845, April.

[55] Ch. Chabrier, Ann. de Ch. et Phys., 1871, (4), XXIII, 161.

[56] Chabrier, Compt. rend., 1871, LXXIII, 485.

[57] S. W. Johnson, How Crops Feed, 1877, 93.

§ 15. *Carbon dioxide.*—The list of organic acids of humus may be closed by *carbon dioxide*, probably the most important of all, and the final and stable product of the decomposition of all the rest. Its nature and that of its important work in chemical geology have been the subject of extensive investigation and are too well known to need any review here. In the humus layer itself, it is derived in part from the atmosphere, and in part from the decomposition of the humus, especially in its superficial layer. Its abundance there is indicated, according to the analyses of Boussingault and Lewy,[58] by the following figures, representing the number of cubic feet of carbon dioxide contained in a layer fourteen inches deep over an acre of soil.

Ordinary atmosphere . . .	12	cubic feet.
Surface soil of forest . . .	57	" "
Sandy subsoil of forest . . .	14	" "
Loamy " " " . . .	28	" "

However, it by no means follows that the solution of inorganic matter, even in soils, must be brought about by this acid: since, as Johnson notices,[59] it has been found that, even in soils rich in organic matter, the water contained only two per cent. of carbon dioxide, instead of one hundred per cent. or its own bulk, its normal solvent power at 60° F.[60] By a known law, the presence of other diffused gases has in this case hindered its solution. In his two brief but interesting papers[61] on the behavior of humus-materials toward minerals, and influence upon their solubility and alteration, Senft has pronounced decidedly that there must be other fluids, besides the solution of carbon dioxide, which produce the alteration of minerals, the decomposition of species which are insoluble in pure and carbonated waters, and even their re-deposit in an unaltered condition. The fluids of chief efficiency he believes to be solutions of the alkaline (especially ammoniacal) salts of ulmic, humic, crenic and apocrenic acids.

For these among other reasons, it appears that, in the infiltrating solutions which are carrying on the chemical alteration within the underlying strata, an undue prominence has in very many

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[58] Mém. de Chim. agric., 369.

[59] S. W. Johnson, How Crops feed, 221.

[60] De Saussure, Rech. chim. sur la Vegét., 168. Also Van den Broek, Ann. d. Ch. u. Ph., 115, 87.

[61] Zeits. d. D. geol. Gesells., 1871, XXIII, 665, and 1874, XXVI, 954.

cases been assigned to the action of carbon dioxide, in comparison with or in entire disregard of the work of its associates. Senft has explained (*loc. cit.*) that the solutions of the other humus-acids are readily converted by a natural decomposition, constantly in progress, into solutions of carbon dioxide. This fact appears to me to show another important office served by the former, in *acting as carriers of carbon* to lower depths. There, by gradual oxidation, they yield a supply of carbon dioxide for chemical work, where perhaps thermal conditions might have prevented its entrance in ordinary carbonated solutions. Illustrations of this fact may be found in the thermal and therefore non-aerated water of St. Allyre, near Clermont, France, which contains 0.0046 per cent. of crenic and apocrenic acids combined with iron, and even 5 per cent. in its deposit of travertin: also in the thermal waters of Luxeuil, France, which deposit a travertin containing 1.02 per cent. of crenic acid.[62]

IV. CONDITIONS OF EXISTENCE.

§ 16. *Genesis of the humus acids.*—The conditions which affect the genesis of the humus-acids have yet to be carefully studied. It is sufficient here to remark that they belong chiefly to three classes. First, the *materials* supplied for decomposition must depend upon the flora of the locality, which may vary with latitude, elevation above the surface, and local conditions of climate. Secondly, the *nature of the decomposition* will be chiefly affected by climate, exposure to sunlight, and amount of aeration. For example, it may be expected that in a comparatively warm, moist climate, with an atmosphere rich in ozone, and a layer of humus resting upon a porous stratum, the most rapid and highest oxidation will be carried on, and yield the largest product of the most complex and freely soluble acids; while, on the other hand, in a dense swamp or heavy forest, in a cold climate, a large part of the humus will remain insoluble, and a *relatively* small proportion of certain acids will be formed. Lastly, the *transference* and destination of the products of decomposition will chiefly depend upon the rainfall, as the agent of transport; upon the temperature, as affecting both the movement of meteoric waters and the permeability of the surface; upon the topography, as determining the rapidity and direction of the flow of sub-aërial streams; and upon

[62] Roth, *op. cit.*, I, 583, 590.

the lithological character of the superficial strata, as conditioning the subterranean absorption of the solutions from above.

§ 17. *Duration of the humus acids.*—The duration of these acids, both in existence and in chemical action, is also affected by a great variety of conditions similar to those already mentioned. Except where vast periods of time have been allowed, no extensive or deep-seated effect may be assigned to their action, in geological work, unless the circumstances have been such as to afford them in large and constant supply, in dissolved and most erosive form, and in favorable application to soluble and porous masses of rock. But on account of their extreme instability, through their rapidity and ultimate certainty of complete oxidation, it must always occur that, however great the work they have accomplished, *the acids themselves have with rare exceptions completely disappeared.* A portion of the carbon remains locked up in the beds of coal and graphite; and a still less amount, now and then, as a carbonate; or a trace of azo-humic acid may be represented in the "empyreumatic odor" of the distillate of some mineral; or even such acids as humic and crenic may remain imprisoned in the tenacious hold of deposits of ferric hydrate or of manganese oxides, of recent age or close subterranean envelopment. But the greater portion of the substance of these erosive agents has returned to the atmosphere; and it is for this reason, I think, that their geological work has been underrated, or attributed, to an excessive extent, to a single member of the group — carbon dioxide.

V. NATURAL SOLUTIONS.

§ 18. *Various investigations.*—The solutions occurring in nature which serve as the agents of transference of the acids of humus to their various fields of chemical action, the identity of the acids in each menstruum, their amount, the nature of their combinations with bases, and the alterations they undergo, have already been the subject of careful enquiry by many analysts. The waters of bogs and peats have been examined by Liebig and Vohl; those of springs and mineral waters, by Lersch, Kersten, T. S. Hunt, C. F. Chandler, etc.; and those of rivers by Ste. Claire Deville, Hunt, Peligot and others.

From the works of Johnson, Liebig, etc., the following table has been compiled, showing the *percentage proportion of silica* in the total amount of solid matters obtained, by various analysts, in solutions of natural products, viz.: in aqueous solutions of 22 soils (Krocker, Way, Zöller, E. Wolf, Grouven, etc.): in a solution of decaying moss (H. Vohl): in a solution of saltmeadow muck (Harms): in a bog-water at Munich (Liebig): and in an artificial solution of peat (R. Hoffman).

Soluble Silica.

Soils, average	5 : trace to 28.	Percentage in residue of water-solution.
Decaying moss	17.	
Saltmeadow muck	4.	
Bog water	3.	
Peat	trace.	

The connection of the solvency of silica with the dissolved humus matters has been generally recognized; but these figures suggest that the solution of silica in natural waters is effected, not so much by the constituents of black humus as by those of the brown or ulmine, *i. e.*, by the vegetable matters in a state of active decay and rich in nitrogen, in *a thin upper layer* of soils, forest-litter and peat-bogs, which is leached out by waters flowing over the surface. Bouis found a large amount of silica in the albuminoids of mineral waters, even 80 per cent. in *glairine*, which contains less nitrogen than the other organic matters, and is not a true albuminoid. Such a substance may generally act as the medium for the solution of silica, afterwards transferring it to the products of higher oxidation, such as the azohumic, crenic and other acids.

A partial confirmation of this theory appears to be furnished by the extraordinary richness of the waters of the marshes and of the subsoil of the Landes, near Bordeaux,[63] both in albuminoid organic matter (0.041 to 0.186 gramme to the litre of water) and in silica and oxide of iron (0.016). The district is underlaid by an impenetrable layer (called "alios") of siliceous sand aggregated by vegetable matter. The amount of albuminoid matter decreases in the subsoil waters with their depth below the surface of the soil: those resting upon a layer of "alios" at a depth of 1 or 2 metres ("eau aliosique albumineuse") containing 0.186, while

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[63] Fauré, Ann. de Ch. et Phys., 1853, (3), XXXIX, 85.

those at a depth of 3 to 4 metres ("eau aliosique") contain only 0.105 gramme.

§ 19. *Humus acids in river-waters.*—In rivers it has been pointed out by Hunt that an intimate connection exists between a hydrographical basin abounding in humus, and a large content of dissolved silica in the river-water;[64] and he illustrates the statement by a reference to two rivers (italicized below). The subject needs a more extended illustration here, to suggest the amount of transference of silica by organic acids to the coast. The following table has been compiled therefore from the best published analyses, by Deville, Frankland, Maumene, Peligot, Chandler, H. Wurtz, etc. Deville found silica to be present in all the waters analyzed, as well as organic matters, often containing crenic and apocrenic acids; he refers the color of the waters, blue, green, or yellow, to the amount of their content of organic matters, but not the solution of silica: this he considers as probably effected by a little alkali, either free or as carbonate.[65]

The figures below show the percentage proportion of silica in the total amount of *inorganic* solid matters in the waters of each river. Except in the case of the Thames, where a full series is presented, and that of the Nile, where the sample was taken at a great distance (2 hours) below, no analytical results have been admitted which have been obtained from samples taken below large cities: since the influence of sewage, the waste products of manufactories, etc., would have vitiated the application of such data to our present purpose. The *absolute* amount of silica conveyed is of course by no means represented by these figures.

Silica Dissolved in River-waters.

Exe (Exeter)	*trace.*	Mohawk (Schenectady)	5
Rhine (Cologne, 1870)	0.2	Thames (Barnes)	5
Cetinje (Dalmatia)	0.6	Severn (Wales)	5
Danube (Buda Pesth)	0.8	Rhine (Bonn)	5.2
Arve	0.9	Hudson (Albany)	5.4
Vesle (Chateau d' Eau)	0.9	Thames (Lambeth)	5.7
Aar (Berne)	1.2	Rhine (Arnheim)	6
Rhine (Basle)	1.3	Dee (Aberdeen)	6.3
Suippe (Rheims)	1.3	Doubs (Riotte)	6.9
Thames (Twickenham)	1.4	Maas (Bocholt)	8.9
Dwina (Archangel)	1.7	Maas (Hocbt)	9
Maas (Grave)	2	Passaic (Belleville)	9.2
Schuylkill (Philadelphia)	2	Seine (Berry)	9.6

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[64] *Op. cit.*, 1878, 126, 150.

[65] H. Ste. C. Deville, Ann. de Ch. et Ph., 1848, (3), XXIII, 32-38.

Main (Offenbach)	2	Maas (Pierre Bleue)	10
Isère (Grenoble)	2.1	Croton	10
Thames (Kew)	2.3	Don (Aberdeen)	10.6
Seine (Paris)	2.7	Delaware (Trenton)	14.9
Clyde (Glasgow)	3	Passaic (Newark)	15
Marne	3.3	Nile (below Cairo)	16.1
Thames (Ditton & Greenwich)	3.3	Moldau (Prague)	16.7
Lütschine (Grindelwald)	3.7	Parana (above mouth)	19.9
Thames (Red House)	3.8	*St. Lawrence* (Vaudreuil)	23
Spree (Berlin)	3.8	Yonne (Avallon)	24.7
Danube (Vienna)	4	Garonne (Toulouse)	29
Ouroy (St. Denis)	4.2	Loire (Orleans)	30
Elbe (Hamburgh)	4.2	Máhanadi (Cuttack)	32.5
Maas (Arendonck)	4.3	*Ottawa* (St. Anne's Rapids)	33.7
Weichsel (Culm)	4.5		

Along the St. Lawrence "the granite of the main and islands is almost everywhere covered with peat, full of stagnant ponds of dark bog-water;" while the Ottawa "drains a region occupied chiefly by crystalline rocks, covered by extensive forests and marshes."[66] With the river Dee "the bounding ridges of the valley are mostly granite and gneiss," and only a small proportion of clay and peat occurs in the valley; the river Don rises in mossy ground and passes finally through alluvial meadows, assuming a brown color from peat.[67] The swampy sources or marshy banks of the Nile, Passaic, and other rivers, are well known, as well as the peaty rock-basins of the glaciated surfaces which drain into such pure waters as those of the Croton, Delaware, etc. The river Máhanadi drains "a sparsely cultivated forest country."[68] Along the Croton river, "swamps occur in some portions of the watershed, where the waters linger on peaty deposits" (C. F. Chandler). In other river-waters, however, only a trace of organic matter has been found in solution, but the percentage of silica in the residue is large: *e. g.*, the Schuylkill (9 to 15 per cent.),[69] the glacier-rivers, Möll (29.8) and Oetz (32.5), the Uruguay (46.4),[70] etc.; in such cases the solution has been effected by the water itself or by alkaline salts.

Without further considering the varied influence of local conditions, etc., it is sufficient to notice the usually low percentage of silica dissolved near the issue of the head-waters from a glacier, or from a rocky watershed, especially where the latter is underlaid by

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[66] Hunt, Essays, 126; Bayfield, Trans. Geol. Soc., 1840, (2), V, 99.

[67] Dr. J. Smith, Jour. Ch. Soc., 1852, IV, 125.

[68] E. Nicholson, Jour. Ch. Soc., 1873, (New Ser.), XI, 229.

[69] M. H. Boyé, Am. J. Sci., 1850, (2), IX, 123.

[70] J. J. Y. Kyle, Ch. News, XXXVIII, 28.

strata deficient in silica; its increase with the flow of the river, especially through cultivated lands; and its excess, where the banks are rich in siliceous sands and in humus, either from peat-bogs or from high cultivation, and where the current is slow.

But this solvency of silica is, so far as due to organic matter, evidently dependent upon combination with organic acids like the azo-humic of Thenard, and proportionate to their amount. The original analyses also show that the amount of "organic matter" in solution may often be large, without a corresponding increase in that of the dissolved silica, probably and chiefly because little of the former has been in the exact condition to accomplish the solution; but a large amount of dissolved silica is almost always accompanied with a large amount of "organic matter."

§ 20. *Humus acids in mineral-waters.*—The same agency is suggested by the presence of dissolved organic matter in subterranean waters, as detected by analysis on their issue as common or mineral springs. Both in the waters and in their subaërial deposits, the proportion of "organic matter" is notable, 1 or 2 per cent. in the case of the tufa of the Springs of Saratoga, N. Y.; but only in comparatively rare instances has the exact character of this constituent been determined by the analyst: *e. g.*, the small amount of apocrenic acid in the "sprudelstein" deposited by the Carlsbad Sprudel-spring (Ragsky: *vide* Roth, *op. cit.*, p. 579). Yet both its tendency to combine with silica, and its acid nature, have been quite certainly established, and should be considered in calculations of the proximate combination of the other constituents; the absence of such consideration may have had a bearing upon some past discordance in the results of mineral-water analyses.[71]

The presence of organic matter in the thermal waters of Reickumer, in the hot springs of Iceland, etc., has convinced Bischof that "organic substances must play an important rôle particularly in the formation of mineral springs;" this he illustrates by the observation that "crenate of soda and crenate of lime possess the power, not only to dissolve a certain quantity of carbonate of lime, but also to protect a perhaps greater quantity of the same from precipitation during the expulsion of carbonic acid

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[71] For example, perhaps, in that of the Trefriw mineral water, Ch. News, 1875, XXXI, 27.

by heat" (Erd. Jour. f. pr. Ch., 1834, II, 70–72, 80). It has been already suggested, that, in this group of organic acids and the other soluble organic matter of less certain character, we have a carrier of carbon to subterranean depths and thermal conditions it could not have reached in the form of carbon dioxide. It may also be that, by the slow but sure subterranean oxidation of these acids, as well as by their action upon limestone-strata,[72] vast quantities of carbon dioxide must be continually evolved, expelled by the temperature of the solutions to higher and cooler horizons, not only producing an extensive chemical erosion and alteration of the rock-material, but often collected under strata impervious to gases, and finally escaping through fissures, joints and faults. In this way may have been effected, in many cases, *the saturation of mineral-waters by gaseous carbon dioxide*, as well as its concentration and pressure indicated by the spouting through the artesian borings for water and oil. Undoubtedly in other cases, the source of the gas must be found, according to the accepted theories,[73] in its evolution from the interior of the earth, or in the reaction between silica and calcium-carbonate, etc. In the case first mentioned, the source of the dissolved organic matter, which, according to my hypothesis, has generated the carbon dioxide or other organic acids, may be found in some subterranean supply: *e. g.*, in the artesian wells of Trafalgar Square, London, the remarkably large amount of organic ("extractive") matter in the deep well-water (0.00096 per cent.), it is stated, "evidently arises from the remains of organized beings which have invariably been found in the Chalk."[74] But the dissolved organic matter may have, in other instances, a superficial origin; such a connection has been already inferred in the mineral-waters of Chambly, Moscow, Forges-les-Eaux, etc., and, in this country, we may yet have to look to the abundant peat-bogs of Saratoga, N. Y., and its vicinity, not only for the contribution of an important group of solvents—the humus-acids—of the bases found in the mineral-waters of that region, but also for the supply of the material for the carbon dioxide gas whose saturation produces their effervescence.

It has been found that the unctuosity of thermal waters, con-

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[72] Hermann thus accounts for the carbon dioxide in the Moscow-water (Erd. Jour. f. pr. Ch., 1842, XXV, 208).

[73] Bischof, *op. cit.*, I, 53, 217, 236. Hunt, *op. cit.*, 8, 102, 112, 148.

[74] F. A. Abel and T. H. Rowney, Jour. Ch. Soc., 1849, I, 102. See also Hunt, *op. cit.*, 152; and R. Brandes, *loc. cit.*, 105, etc.

taining sodium sulphide, is produced by substances styled glairine, hydrosin, baregine, or "zoogene, formed of microscopic algæ, related to Hygrococis and Leptothrix," which contain a considerable proportion of silica, even over sixty per cent. In the analyses of the waters of ordinary and mineral springs, artesian wells, etc., there have been very generally reported traces of albuminoid matter, dissolved humus, asphalt, petroleum, resin, animal matter or mucus, humic extract, etc., which must probably serve as the crude materials for the constant supply of the organic acids generally associated. Of the occurrence of the latter, reported in published analyses of mineral-waters, I have compiled the following list from numerous sources, mostly well-known.

Humic acid, in the mineral-waters of Wurtemberg; *e. g.*, a trace in the Soden, Winklerbrunnen (Schweinsberg); 0.12 grain in 16 oz., Steben (Vogel); 0.157 grain, Konigswarth, Trinkquelle (Berzelius); 0.065 grain aluminum-humate, Giengen, near Brenz (Salzer); mineral-water of Tatenhausen (R. Brandes, Pogg. Ann., 1830, XIX, 98).

Crenic acid, traces in the mineral-waters of Ronneburg (Döbereiner); as ferrous crenate, in the springs of France, at Audinac, Ariége (Filhol), Campagne, Aude (Filhol), Chateauneuf, Puy-de-Dome (Lefort), Condillac, Drome (O. Henry), Vittel, Vosges (Henry), Lamotte, Isère (Henry), Martigny, Vosges (Jacquemin), Rennes, Aude (Henry), Lamotte-les-Bains, Isère (Henry); 0.002 gm. to the litre, Coise, Savoy (P. Morin); 0.02 gm., Saint Pardoux, Allier (Henry); 0.013 gm., Sermaise, Marne (Henry); sodium and ferrous crenate, Bussang, Vosges (Henry); potassium-crenate, Sentein, Ariège (Henry); 0.04 gm. ferrous crenate and carbonate, in Jonas Spring, and 0.017 gm. ferrous crenate, in Thermal Spring, Bourbon-L'Archambault, Allier (Henry); 0.098 gm. ferrous crenate, and 0.002 gm. potassium-crenate, Forges-les-Eaux, Lower Seine (Girardin & Morin, and Boutigny); 0.149 grain of torfocrenic, trace of humocrenic, and 0.235 grain of torfoxycrenic acid, in combination with ammonia and ferrous oxide, in the mineral-water of Moscow, Russia (Hermann); 0.359 grain to imp. gallon, Pitville strong saline water, 0.333 grain, Royal Old Wells No. 4, 16.825 grains, Royal Old Wells, No. 1, Cheltenham (Abel & Rowney); 0.64 grain to U. S. gallon, Chalybeate Springs of Minneapolis (S. D. Hayes),[75] etc.; Birchdale Spring, N. H. (C.

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[75] Geol. and N. Hist. Survey, Minn., 1876, 199.

T. Jackson); Alburg Springs, Vt. (C. T. Jackson); 0.112 grain to U. S. gallon, Highgate Springs, Vt. (A. A. Hayes); 0.039 grain calcium-crenate, and 1.801 grain " crenate silica," Cooper's Well, Miss. (J. L. Smith); 0.312 grain ferrous crenate in the thermal waters of the Warm Springs (A. A. Hayes) and 0.108 grain crenic acid in those of the Healing Spring (W. E. A. Aikin), both in Bath County, Va.; 0.222 and 0.232 grain ammonium-crenate in the two Bath Alum Springs, Va. (A. A. Hayes); 0.455 grain calcium-crenate, and 0.01 grain ferrous crenate, Berkeley Spring, Va. (A. A. Hayes); 0.066 grain ammonium-crenate, and 0.085 grain ferrous crenate, Jordan Alum Spring, Va. (W. E. A. Aikin); 0.63 grain ammonium-crenate, Stribling's Sulphur Spring, Va. (Campbell); 0.4–0.98 grain crenic acid, (0.7–1.401 grain ammonium-crenate), Rockbridge Alum Springs, Va. (A. A. Hayes); etc.

Apocrenic and *crenic* acids, traces; Porla Spring, Sweden (Berzelius); Rochefort artesian water (Roux);[76] Lamalou, Hérault (Moitessier); ferrous crenate and apocrenate, Chateau-Gonthier, Mayenne (Henry); Alleghany Spring, Va. (F. A. Genth); 0.075 grain apocrenic acid to U. S. gallon, and 0.091 grain crenic acid, Bladen Spring, Ala. (R. T. Brumby); 0.002 grain of both acids, Catoosa Spring, Ala. (W. J. Land); ferrous crenate and apocrenate, Seneca Spring, S. C. (W. J. Land); 0.137 grain crenic, 0.099 grain apocrenic, to imp. gallon, Trafalgar Square artesian water, London (Abel & Rowney); 0.243 grain crenic, 0.147 grain apocrenic, Cambray Spring, Cheltenham (Abel & Rowney); 1.025 grain crenic, 1.415 grain apocrenic, Bristol, England (Herapath)[77]; 0.0046 per cent. ferrous crenate and apocrenate, in the thermal waters of St. Allyre, near Clermont, France (Girardin)[78]; 0.00186 per cent. crenic and apocrenic acids, with traces of *propionic* and *formic* acids, in the Eckholtz Spring, Ronneby, Sweden (Hamberg).[79]

Formic acid, trace, in the water nearly saturated with carbon dioxide, Carlsbrunn, Austrian Silesia (Schneider);[80] 0.0048 gm. formic acid to the litre, with trace of *acetic acid*, St. Boes, Pyrenees (Garrigon).[81]

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[76] Jour. de Ph. et Ch., 1872, Feb.

[77] Jour. Ch. Soc., 1850, II, 200.

[78] Ann. d. Mines, 1837, (3), XI, 458.

[79] J. pr. Ch., 1860, 80, 396.

[80] Proc. Acad. Vienna, 1862, Apr. 2.

[81] Am. Chem., 1873, IV, 320.

Butyric acid, trace, Old Crescent Well, Harrogate, England (Fairly).[82]

Mellitic acid (?), *Geic acid*, etc., in mineral-waters of France (P. Labarthe, Les Eaux Min., etc., de la France, 1873, 3).

The survival of traces of acids of such complex constitution may have therefore great significance; and it is important to remember that the presence of even the minute proportion, styled *a trace*, in the waters of a spring of free and constant flow, implies the annual delivery of a large absolute amount.

The use of the term "organic matter," in the thorough examination of mineral-waters, may yet become obsolete, as indicating too gross an imperfection of analysis; and the exceptional cases, in which the organic constituent of waters or solid substances has already been determined with exactness, may yet be searched for by future workers as at last possessing, for certain purposes, an invaluable significance.

The influence of the character and amount of nitrogenous organic matter in solution upon the potability of waters is well known. The suggestive observations of a few analysts hint also at the possible assignment, to the organic constituents in certain mineral-waters, of the subtle agency to which their therapeutic value is due; for example, for the supply of a ferruginous salt in the form most assimilable in digestion, or more directly, if highly nitrogenous, in scrofulous diseases, etc.[83] Instances of the occurrence of such acids in mineral-waters have just been given, and a single illustration of their indirect action will suffice. The Greenbrier White Sulphur Springs of Virginia contain in a gallon, by the analysis of Mr. S. D. Hayes of Roxbury, Mass., 11.29 cubic inches of carbon dioxide. The saline matter in 50,000 grains consists chiefly of calcium and magnesium-sulphates and calcium-carbonate, and also contains,

Organic matter, 3.74; Silica, 1.34, etc.

"The alkaline bases are also in very small proportion, and seem to be united to the siliceous earths in combination with a peculiar organic matter. The organic matter in its physical and chemical character resembles that found in the water of the Red Sulphur Springs, and differs essentially from the organic matter of some

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[82] Ch. News, 1874, XXX, 151.

[83] Boutigny, Compt. rend., 1871, LXXIII, 249; Brandes, *loc. cit.*, 93.

thermal waters. * * * * The medicinal properties of this water are probably due to the action of this organic substance," through the generation of sulph-hydric acid from the earthy sulphates.

ACTION WITHIN LOOSE DEPOSITS.

VI. SANDS AND GRAVELS.

§ 21. *General chemical action.*—The published observations on the chemical action of the acids of humus in nature are rather of limited character, and have hitherto been naturally confined to agricultural chemistry and to the formation of bog-ores. The great work of Bischof, to which reference would naturally be made for information on this subject, is found to be extremely deficient, in view of *recent* investigations; and it seems therefore desirable first to consider briefly those views of this author which pertain to this field. His chief, almost only, discussion of the group of humus-acids is contained in a few pages of the first volume of his work. He describes the general properties and reactions of humic, crenic and apocrenic acids, and states that "in marshes and morasses there is then no want of acids which are capable of dissolving protoxide and peroxide of iron, and Kindler's observations show that such solutions really take place."[84] The only acid or constituent of humus, however, with which he afterwards connects general and actual *solvent* action in nature is carbon dioxide, and this is fully and constantly referred to throughout the work. The influence of "organic matter" is, it is true, frequently considered, but almost always as merely the *reducing agent* of sulphates and higher oxides, preparing the bases for solution in the great menstruum, carbon dioxide (*op. cit.*, I, 52, etc.). In regard to the solution of iron-oxides, he evidently believes that ferruginous waters must be necessarily almost always carbonated, and even states that "hydrated peroxide of iron is never present in water" (II, 467), disregarding the ammoniacal solutions of the crenates, etc., to which he had already made reference (I, 166). In fact, the existence and influence of the double salts of the humus-acids, which now appear to us to be the main agents for initial solution and decomposition, are ignored by Bischof. In regard to silica, he recognizes and frequently refers to "the remarkable affinity of organic matter for silica" (I, 187, 189), and to the view that "organic

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[84] Chem. and Phys. Geol., I, 166.

matter in any combination precipitates silica from its solution" (I, 312), etc.; but for its transport in nature, he constantly resorts to its solvency in natural waters, usually at the ordinary temperatures, which he considers chiefly dependent upon the amount of sodium-carbonate present and never exceeding $\frac{1}{10000}$ (II, 454). The ferrous silicates, which occur in the residues deposited by waters or resulting from their action, and whose existence as such he founds on the presence of silica in iron-ochre, he continually regards as in solution in natural waters and exerting chemical action (I, 4): without reference to the organic media—ferrous silico-azo-humates—which, in all probability, accomplish both the solution of silica and iron and the chemical action of their solutions. He often frankly admits himself at a loss to account for certain phenomena by their action (III, 543, etc.); and notwithstanding therefore the attractiveness of his views on these subjects, on account of the simplicity of the agencies he invokes, later investigations have proved that in nature the agencies, as well as their effects, are highly varied and by far more complex.

From the rather antiquated portion of chemical literature which forms the basis of present views, only those facts will be now selected which bear chiefly upon the conditions *antecedent* to the formation of deposits of hydrated ferric oxides.

A. Kindler[85] observed that decaying roots, traversing ferruginous quartz-sand, absorb the rain-water filtering through, and, by decomposition, yield acids which dissolve the oxides of iron out of the surrounding sand, sometimes to a distance of one or two inches. So that in summer a cylinder of decolorized sand surrounds the root, or even a considerable layer may be so bleached when the root is large and much decayed. "This phenomenon also presents itself in woods and gardens; decolorized sand is found everywhere under rotting leaves . . . If a decaying root and quartz sand, colored with oxide of iron, are often moistened with water, it will be found ferruginous, after filtering and evaporating. This process of decay acts, therefore, as a powerful deoxidizing agent." He supposes that an organic acid has been formed which reduces the iron and dissolves it in the form of a protoxide salt; the latter is carried off by rain-water, is oxidized by the air to an insoluble basic combination, and then deposited

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[85] Pogg. Ann., 1836, XXXVII, 203.

on the bottoms of bogs and morasses into which the water flows. To this observation Berzelius[86] added that he found a bog-earth to contain basic crenate and apocrenate of iron-oxide, that these acids are formed during the decay of plants, and their ferrous salts are soluble in water. In this fact he found one of the means by which iron-ochre is concentrated in lakes and bogs by transference from ores disseminated through soils and rocks.

From the careful observations of Daubrée[87] upon the continuous formation of bog ores in marshes, etc., in the plain of the Rhine and Lorraine, the following quotation may be translated, relating to the initial conditions of the deposit:

"1. The peroxide of iron, intermingled with deposits of little coherence which contain vegetable matters in decomposition, is dissolved by the infiltrating meteoric waters, under the influence of certain products of the decay of these plants.

"2. It is by the action of carbonic acid and crenic acid, that the peroxide of iron, reduced, at least partially, to the state of protoxide by the presence of the contiguous vegetable matter, appears to be brought into a state of solubility in water . . . .

"3. Everywhere where the water of these springs flows slowly in contact with air, it leaves behind, particularly during the summer, a gelatinous mud of a blackish brown color, which is principally composed of protoxide and peroxide of iron, combined with carbonic acid, crenic acid and water. The oxide of manganese is rarely wanting, and its presence is probably due to the same reactions as those of the oxide of iron. The carbonic acid is disengaged in proportion as the protoxide of iron passes into the state of peroxide, and ultimately, after the substance has been dried at the ordinary temperature, naturally or artificially, only traces of this acid remain.

"4. If the precipitate of the spring has been confined several days in its basin, it is in addition intermingled with many siliceous shells of infusoria belonging to the genera Navicula and Gaillonella, as well as very numerous filaments of Oscillaria.

"5. The deposit formed around each spring is transported during high waters into a brook or river of the vicinity; the same thing occurs with that part of the ferruginous combination, which, not having yet been decomposed, has remained in solution. As

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[86] Berzelius Jahresb., 1838, 17, 211.

[87] Compt. rend., 1845, XX, 1775.

long as this brook or this river flows rapidly, it deposits nothing upon its bed; but everywhere, where the rapidity of these watercourses is considerably retarded, particularly in the pools of stagnant water which they supply not far from their beds, the oxide held in suspension, and that which is yet in solution, are little by little precipitated; then the deposit, infiltrating laterally into the sands, proceeds to contribute to the increase of concretions in the form of veins and nodules, which, at the end of a certain lapse of time, become exploitable as iron-ore."

The author further considers the deposits of ore thus produced in bogs and their relation to the associated peat formed under the same conditions, viz., of shallow water renewed constantly but at a very slow rate.

J. F. Johnston also states, in regard to another common result of the vertical percolation of natural ferruginous solutions:

"In sundry districts the decaying vegetable matters of the surface soil are observed to sink down and form an ochreous *pan*, or thin yellow layer, in the subsoil, which is impervious to water, and through which therefore the rains cannot pass. Being arrested by this pan, the rain-water, while it rests upon it, dissolves a certain portion of the vegetable matter, and when collected into wells, is often dark-coloured, marshy in taste and smell, and unwholesome to drink."[88]

The same product has been also thus described: Hardpan is a dense, almost impenetrable, crust or stratum of ochrey clay or compacted gravel, often underlying a fairly fruitful soil. It is the soil reverting to rock, the particles being cemented together again by the solutions of lime, iron, or alkali-silicates and humates that descend from the surface soil. Peat swamps thus exist in basins formed on the most porous soils by a thin layer of *moor-bed-pan*.[89]

Detmer and others have given similar descriptions. Johnson also observes,[90] on the agricultural relationships of the chemical reagents which have produced these natural solutions: "the organic acids of the humus group probably aid in the disintegration of soil by direct action; . . The ulmic and humic acids themselves, according to Mulder, indeed do not exist in the free state

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[88] The Chemistry of Common Life, 1876, 36.

[89] S. W. Johnson, How Crops Feed, 1870, 156.

[90] *Idem*, 139.

in the soil, but their soluble salts of ammonia, potash, or soda, have acid characters, in so far that they unite energetically with other bases, as lime, oxide of iron, etc. . . The same is probably true of crenic and apocrenic acids."

§ 22. *Induration of calcareous sands.*—The high content of carbon dioxide in seawater, which has been found[91] to be dependent upon the magnesium and calcium sulphates in solution, has produced within the tropics, in spite of the elevated temperature, a partial solution and cementation of the coral sands, resulting even in the consolidation of beaches. These commonly occur in many islands of the Atlantic,[92] *e. g.*, Madeira, St. Jago of the Cape de Verdes, Ascension, St. Helena, etc.: of the Pacific, *e. g.*, in the Paumotus, Navigator and Hawaiian groups:[93] of the West Indies, *e. g.*, Guadaloupe, Sombrero, etc.: along the coast of Brazil:[94] and of vast extent on the Australian shores. Even in some of these cases, however, Hartt indicates his suspicion that the solidification has been affected by the percolation through the beach of the "black waters" from the inner lagoon;[95] and this seems the more likely from the recent discovery of a second indurated layer at a depth of about 18 feet,[96] unless this may have been produced simply by subsidence of the coast. The drift sand-rock or "Æolian formation" of consolidated calcareous sand-rock, which constitutes the Bermudas and the islands of Oahu and Kanai in the Pacific,[97] has had certainly no connection with the carbon dioxide of seawater, but only, according to R. J. Nelson[98] and Wyville Thomson,[99] with that of falling rains. The warm rains can carry but a small content of that gas out of the atmosphere, and yet the work continually in progress in the Bermudas, in the consolidation of the blown sands, in the excavation of caverns, in the formation of the huge stalactites and concretions, etc., indicates an enormous and constant supply of solvent. That this is largely generated within the layer of soil (which contains

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[91] J. Y. Buchanan, Proc. Roy. Soc., 1874, 483; also, Depths of the Sea, 115, 343, 518–9.

[92] C. Darwin, Geol. Obs., 1876, 56, 98, 161.

[93] J. D. Dana, U. S. Expl. Exp., Geol., 1846–1849, 44, 148, 153.

[94] C. F. Hartt, Geol. and Phys. of Brazil, 1870, 107, 113, 179, 342–345.

[95] Hartt, *op. cit.*, 115, 343.

[96] J. C. Hawkshaw, Geol. Mag., 1879, New Ser., VI, 91.

[97] Dana, *op. cit.*, 45, 64, 254, 277.

[98] Trans. Geol. Soc., 1840, (2), V, 103.

[99] Voy. of Chall., Atlantic, 1878, I, 292.

about 15 per cent. of organic matter), though partly from the organic component of shells and corals, seems to be more definitely shown by the strata abounding in tubular deposits around rootlets (Nelson, *loc. cit.*, 110–111), by the particles of black carbonaceous matter as well as the organic membranous tissue still remaining in the shelly sand, and by the relationship of the soil to the deposits of "red earth," covering the surface to the depth of about a foot (Nelson, *loc. cit.*), especially, according to Thomson, *in the hollows.* In this the proportions of vegetable matter are less but variable: the soil, according to the analyses of Buchanan, containing about 20 per cent. of siliceous sand and 51 per cent. of ferric oxide and alumina; while, in the red earth, the amount of sand rises to about 31 to 40 per cent., and that of the bases just mentioned has been leached out down to 26 and even 17 per cent. The process appears to be analogous to that which has yielded a part of the "red clay" of the deep sea ooze, the organic acids of the soil having dissolved the calcium-carbonate out of the superficial layer of coral-sand, and concentrated, to the degrees above stated, its content of silica (0.05 per cent.) and of the same earthy bases (0.52 per cent.). The occurrence of "a small quantity of manganese" in the red earth is a suggestive fact, noted by Nelson, in his list of the few minerals found in these islands (*loc. cit.*, p. 105). At Raine Island,[100] one of the New Hebrides in the Pacific Ocean, a reddish tint affects the calcareous sand and its consolidated crusts, "immediately above the beach-line, where the grass commences," and probably indicates the incipient attack of the same solvent agency. Calcareous sands are also sometimes found consolidated into crusts around decaying stems of plants,[101] and left projecting as hollow tubes by the decay of the wood and removal of the loose sands.

§ 23. *Induration of siliceous sands.*—The loose Tertiary sands of the north of France exhibit a remarkable cementation, locally, by calcium-carbonate and by silica;[102] and a similar cementation of sands and gravels by ferric oxide has been observed at many localities in the valleys of the Rhine and Ahr.[103] All these proc-

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[100] H. N. Moseley, Notes by a Nat., 1879, 347.

[101] At Cape of Good Hope, Moseley, *op. cit.*, 149; in Australia, C. Darwin, Jour. of Res., 1871, 540.

[102] Jukes, Man. of Geol., 121.

[103] Bischof, *op. cit.*, German ed., 1863, I, 565.

esses have probably been effected by the percolation of solutions of lime, iron-oxides, etc., in the salts of the humus-acids, etc. The bleaching of ferruginous sands by the same action, when they are rich in plant remains, has also been studied in the Brown coal and Cretaceous formations of Germany.[104] I have recently given elsewhere a description[105] of indurated layers of sand and gravel in the Tertiary and Cretaceous areas of New Jersey, with a resumé of the similar recorded observations. Their cause was assigned, in the New Jersey sands, to certain of the more soluble humus-acids, not yet exactly determined, whose continuous formation appears to be favored especially by the nature of the exuviæ of the pine, the warm moist climate of the region, and the porous aerated strata below. The oxide of iron, leached out of thick layers of the yellow sand, is deposited and concentrated within the interstices of alternating layers of the coarser sands and gravels, indurating them into a compact and generally conglomeritic sand-rock. This latter process is found to have been increased, if not occasioned, by the presence of the abundant pebbles of a yellowish chert, which have been partially and indeed largely replaced by iron-ochre, while the crystalline and even chalcedonic varieties of quartz have been unaffected. The former have been evidently derived from the chert layers of a Devonian limestone; and if their amorphous material was originally segregated there, as I shall explain beyond, by the action of organic acids akin to those of humus, it is easy to see that their present molecular condition, as well as porosity, has rendered them easily re-soluble in a similar solvent.

Now carbon dioxide, and indeed many other of the humus-acids, could have had little to do with this solution; the humic and azohumic acids can alone solve the problem, and it is probable that these have predominated in quantity among the group of organic solvents which have percolated through the sands and reduced and leached out the ferric oxide in ferrous combinations. The heavy deposition of hydrated ferric oxide chiefly in the coarser layers, especially the gravels, seems to imply an oxidation occasioned in part by the large air-spaces among the pebbles. But the substitution of the same substance in place of the chert indicates

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[104] *Idem.*, 566–7.

[105] "On the Induration of Sands by Ferric Oxide, and its Precipitation by Chert."

apparently the peculiar efficiency of these acids, for the solution of silica, in their *nascent condition*, on the partial separation of their oxidized base. The large amount of the ferric hydrate, which was consumed in the cementation and complete induration of these gravels, appears therefore to have been yielded through its abundant separation in the presence of the chert; in the absence of that substance, it is probable that the ferric oxide would ultimately have been mostly conveyed, unhindered by the gravel, to lower levels of drainage or into the basins of sub-aërial deposit as bog-ores. These phenomena therefore seem to indicate that the strongest solvents of amorphous or colloid silica in nature consist of a group of certain organic acids of humus, when separated from ferrous oxide by its higher oxidation: perhaps, also, that the silico-azo-humic acids thus formed enter into little or no combination with ferric oxide. Probably during further conveyance through the sands, these silicated organic acids are accompanied in solution with sufficient organic matters to reduce and bring into combination a new burden of iron-oxide. It is not always safe to attempt by field observation to anticipate the chemical reactions of little known substances; and we must look forward for exact and certain information on this subject to the full publication of the long-promised results of Thenard's investigation.

It may be further remarked, in reference to the continuous supply of air for the oxidation just described, in subterranean cavities, that the percolation of waters through such bodies of sand is always intermittent, being chiefly dependent upon the repeated showers of rain upon the surface. The effect of each mass of water, percolating after a shower, must be ultimately to draw down *with it* the gaseous atmosphere of the sands, rich in nitrogen, and *after it*, by atmospheric pressure and capillary attraction, new supplies of pure air from above. Though the mass remains almost constantly damp, through the occupation of the finest interstices by capillary moisture, there are natural vertical channels for the main percolation, apparently shown in the fibrous variety of sand-rock with vertical tubes, through which the drainage is mainly conveyed in the endless repetition of the foregoing process. The destination of the solutions, now rich in silica, will be the subject of further investigation.

§ 24. *Purification of Beach Sand.*—The purity of the sand and the whiteness of the dunes, along the New Jersey coast,[106] have been the subject of frequent remark by the passing traveller and artist. The same characteristics probably prevail along the whole ocean front, from the dunes of Cape Cod to those of the Carolinas. But this whole tract consists of a definite series of belts, passing from inland to the beach, viz.:

First, a loose mass of ferruginous sands, with some clays:

Secondly, a broad fringe of fresh-water swamps and peat-bogs, passing gradually into salt-marshes, rich in acid solvents, upon the surface; and underneath, at a slight depth, frequently an indurated layer of cemented sand-rock or hard-pan:

Thirdly, a long sea-channel or inner bay, swept by the tidal currents, by which all drainage solutions and suspended impurities from the land are constantly scoured out into the sea:

Fourthly, an interrupted narrow fringe of marshes, lining the inner side of the beach: and

Lastly, the long, narrow beach of pure siliceous sand, washed up by the waves and blown about by the winds. On examination of this sand at several points of the New Jersey coast, from Egg Harbor Inlet to Sandy Hook, I have found it to consist almost entirely of rounded and sub-angular granules of limpid, white, and reddish quartz, basanite, and polished black iron-sand, possessing no magnetic attraction.

The inner bay, with its fringing deposits of decomposing humus, therefore forms a great acid basin or vat for the digestion and purification of the ochreous sand. This purification has, I believe, been hitherto attributed to mechanical attrition under the action of the surf, and has been disguised by the black and fetid muck of the salt-marshes which envelopes the siliceous grains. But beneath or intermingled with the superficial mould under every pine and cedar forest on the land, and underneath the current of flowing water in every ditch through the marshes, gleams out exactly the same intermixture of white quartz-sand, with a little black iron-sand, as the winds and the waves toss back and forth upon the outer beach; and, in the latter, Cook reports, in addition to grains of quartz and iron-sand, only about one per cent. of

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[106] Also on the coast of Brazil, according to Hartt, *op. cit.*, 380.

bases, probably "introduced in the form of dust by winds and storms."[107]

That purification of the sand therefore, to which is due its mobility under the agency of water and wind, as well as the absence of ochreous silt which might prove deleterious to submarine life along the shores, has been produced by chemical action, the solvent cleansing work of these organic acids. And there may be the further result that, as in the course of the subsidence of the coast the loose Tertiary deposits are gradually encroached upon by the sea, only the superficial layer of loose and mobile sands is worked up by the waves and blown back by the winds upon the marshes; while the mass of the formation beneath is protected in large degree by the extensive layers of hard-pan. The action of the salt-marsh differs from that of the peat-bogs which lie next to the land, not merely in the completion of the solution of iron-oxides in the sands, but in their reduction to sulphide, at least in part, in presence of the sulphates of the sea-water and the decomposing vegetable matters, as long ago pointed out by Bischof, Dawson, and others. It therefore follows that the iron-oxide, though largely brought into solution out of the sands by the acids of humus, is but in small part swept down into the sea. Part of it is soon precipitated and stopped, in the form of bog-ore beneath the swamps, and of the ochreous hard-pan beneath the soil. The remainder is conveyed by the streams and drainage into the bay; but the office of the marshes is to detain it and again deposit it in insoluble form. And in that form it seems to be finally in greater part lowered down into the ocean bed, during the course of the subsidence of the coast.

These basins of chemical erosion are well represented, along our Atlantic border, by those local charts which show the marshes, and along that of New Jersey, by the map on "Economic Geology" just issued (1880), by the State Survey. This map presents clearly the area of the band of salt-marshes, along the Atlantic front of that State and up Delaware bay. In the accompanying wood-cut I have given an ideal cross-section of the marsh-deposit, across the inner bay, on the coast of Ocean county, N. J., from the edge of the meadows or fresh-water swamps to the

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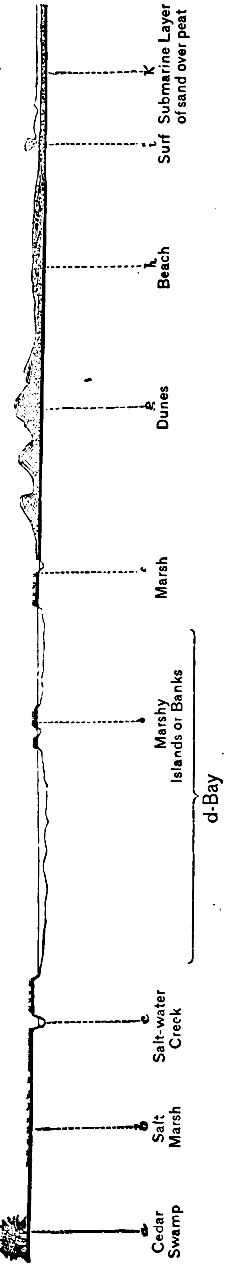
[107] Rep. Geol. N. J., 1863, 386.

ocean. At *a* is the edge of the cedar-swamp, and it is interesting to notice that on thrusting anywhere through the springy moss bottom of the swamp into the clear brown water, a few inches underneath, the latter is found to be in steady motion, flowing at an appreciable rate toward the bay. Next comes the salt-marsh, *b*, overflowed by the higher tides over an area indicated by the predominating salt-grass. The fresh-water streams from the uplands pass into the natural creeks, *c*, which intersect the marsh. Their bottoms are covered by the black marsh mud, sometimes mingled with shells from ancient mounds or shell-heaps, which have been carried down, in the course of the gradual subsidence, within the reach of the tides. Wherever, however, the force of the current is sufficient, the bottoms of these creeks and especially of the artificial ditches in the salt-marsh are covered with white sand, intermingled abundantly with the siliceous valves of diatoms. The section next presents, though on a too contracted scale, the shallow waters of the bay, *d*, interspersed with islands or submerged banks, *e*, which represent fragments of the original salt-marsh. The outer beach is also underlaid by this, sometimes projecting as a fringe, *f*, uncovered by sand, on the inner side; its centre is occupied by the dunes, *g*, with the usual irregular cross stratification; and beyond comes the beach, *h*, in which the thinly laminated sand-layers incline gently (at about 9°) towards the sea — the structure in both dunes and beach being accentuated by the sorting out of the black grains of iron-oxide by wind or water respectively. Beneath the surf the beach-sand is continued in a thin layer, which, after a violent storm, is sometimes stripped off, together with portions of the beach itself: so that, at such a time, one may stand upon the beach



and look down upon the black, marshy surface, usually concealed beneath the sea and sand. This sometimes still retains the hoof-prints of cattle which formerly grazed upon the marsh when above the sea-level, now in long lines which descend toward the depths of the open ocean and which present an impressive illustration of the progressive subsidence of the coast. All along this beach (as far to the northward as Long Branch, according to Prof. D. S. Martin), the force of the waves, during storms, has been sufficient to tear up fragments of the submarine peat-bed, which are found scattered above the surf-line and are often penetrated by boring-shells. Where the outer beach has advanced, by the heaping up of the sand by surf and wind, the salt marsh, more or less intersected by creeks and the inner bays, may extend from one to six miles in width, projecting inwards along the streams to far greater distances and so passing gradually into the swamps of the uplands. At other points, the tidal currents have swept away to seaward all this band of loose, purified deposits, and the surf beats directly upon the mass of ferruginous sands. And thus by intermittent advance and recession, these chemical and mechanical agencies alternate in their work for the common end—the purification of the littoral deposits of sands and clays.

VII. Action Upon Clays.

§ 25. *Champlain Clays.*—The distinction of the Champlain clays into "blackish-blue, bluish-grey" and "yellowish-grey, greyish-white" seems to have been first made in the Hudson Valley, in a paper by John Finch,[108] and afterwards by Eaton.

In the geological survey of the State, Mather gives full and precise descriptions[109] of the two layers of clay, under the names "grey or buff-colored" and "blue," and points out the invariable superposition of the former in New York, with the "line of junction generally very distinctly marked," but a more irregular arrangement of the same clays in Ohio, Illinois and Michigan. He also describes (*l. c.*, p. 251) similar differences in color between the upper and lower layers of the Tertiary clays of Long Island. Along the bank of the Hudson, these deposits are very thick, often over 180 feet; and at Newburgh, I observed the upper layer of the clay beds, to a quarter of their depth, to be much mixed

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[108] Am. J. Sci., 1826, X, 227, 229.

[109] Nat. Hist., N. Y., Geol., 1843, Pt. IV, I, 125, *et seq.*

with fine sand, in very delicately laminated layers, and to present a light-reddish to brownish tint. The lower and predominating mass is of a bluish-green color, while moist, and furnishes the chief material for the brick-yards. The upper layer is stated to be too "fat" or rich, evidently in alumina, for this manufacture, when used alone, and is mixed with the lower in the proportion of one to three parts of the latter. At other points along the bank of the river, for at least two miles northward, the same alteration was observed. Occasionally the formation of a calcareous conglomerate occurred, in thin horizontal seams, where a trickling solution, probably derived from some marly layer, issued at the edge of the stratum, through a lens of gravel, and deposited its calcium-carbonate as an amorphous cement around the pebbles. It seems likely that wherever, as at some localities in Massachusetts, the cement of such a conglomerate is *crystalline calcite*, the solvent has been probably carbon dioxide alone; while its amorphous condition in this case may indicate, as with similar deposits in peat-bogs already referred to, the solvent action of the colloid acids of humus. In New Jersey, according to Cook's reports, a similar superposition occurs of white, buff, or red, over blue clay, in beds of Champlain age.

An interesting section of the gray and blue clays has been mentioned to me by T. B. Brooks of Newburgh, as occurring in a railroad-cut near Oxford, in Orange Co., N. Y., the line of demarcation between the two clays being mainly parallel to the contour of the hill, though deeper along the centre, where naturally the drainage was slower and the material longer attacked. In 1861, E. Hitchcock first made the distinction, in the Champlain deposits of Vermont, between the brown and blue clays and their relative superposition. He also gives an analysis of the brown clay, by T. S. Hunt, and states his own opinion that "the difference is accidental, perhaps from weathering."[110] Since then, C. H. Hitchcock has made a very careful study of the similar deposits in New Hampshire.[111] He finds that the gray clay occurs to a depth of even fifty-six feet from the surface, in beds which are sometimes sixteen to twenty-seven feet in thickness, or even thirty-eight feet when sandy. Near the top it is compact and inclined to break into small, angular fragments, the sides of which

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[110] Geology of Vermont, 1861, I, 157, 161.

[111] Geol. of N. H., 1878, III, 94, 163, *etc.*

are stained with films of iron-ochre. Below, it is sometimes separated by a thin layer of sand, from the blue clay, and sometimes "changes gradually near the bottom into blue clay" (*l. c.*, pp. 154, 155). At Rochester occurs what he terms an "anomalous section" (*l. c.*, p. 155), and which is in fact the most satisfactory in determining that the relation of the two clays is simply one of decomposition. Here the blue clay projects horizontally in a great tongue-like mass into a layer of the gray clay, fifteen feet thick, the lines of stratification being continuous through both.

The same differences, in oxidation of iron and in color, exist in the layers of glacial till, which Hitchcock has distinguished by the terms "Upper" and "Lower;" and he suggests that the differences may have been produced by derivation of the blue clay from the lower till, and the gray from the upper till or from the washing of the upper terrace deposits. G. W. Hawes, however, attributes the increase of iron in the clays over the tills, as shown by his analyses (*loc. cit.*, p. 333), to the ready transport of the fine ferruginous material along with the bulk of the clay, and explains the difference in oxidation of the iron in both the tills and clays thus: "if the beds of both till and clay, as first deposited, were of the same nature as the lower beds at present, atmospheric and aqueous agencies would in time produce the differences in both now seen." Nevertheless the division of the till into two classes, by Hitchcock, is probably well grounded, as well as his explanation of their differences; though there is need of a clear distinction between the true upper till and the bleached upper layer of the lower till, wherever the latter is superficially exposed, *e. g.*, at the Geyser Spring of Saratoga, N. Y. On the other hand, in regard to the two clays, all the observations appear to establish the correctness of Hawes' explanation; though I think we can refer to the definite sources of the chemical action.

In regard to both the lower till and the clay the following inferences may be drawn. The entire stratum of each, when first deposited, was substantially of the same nature and composition —that of the layer now found below. The heavy vegetation, which originally clothed the surface, the rich soil superposed, and the percolating meteoric waters, have given rise to solutions of the humus-acids, which have permeated the superficial layers, decomposed the finely divided silicates, and dissolved all readily soluble salts, especially of lime and ferrous oxide, and carried them off.

Although capable of overcoming the density and impermeability of the clay, the action of the solvent seems to have been facilitated to a considerable degree by the numerous intercalations of layers of porous sand; and the present depth of the upper brown layer is the measure of the extent of this alteration and lixiviation, since the original deposit of the stratum.

Jos. LeConte has also shown that the difference between the blue and the overlying red argillaceous gravel, occupying the old river-beds of California, has been due entirely to a similar process of the downward progressive oxidation of the iron.[112]

§ 26. *Cretaceous clays, etc.*—In New Jersey many passing observations[113] on the clays, possibly Cretaceous, indicate the results of a similar process of alteration, often associated however with the results of decomposition of *pyrite* and apparently of the glauconite also. In these beds the white or light-colored sands and pipe-clays (sometimes blackened by carbonaceous matters) generally overlie others of darker shades of blue and brown, or are sometimes intermingled with them, when intercalations of porous sand-beds occur. Sometimes the blue clay is mottled or spotted with irregularly mixed red and white masses, or stained near the surface by oxide of iron in filmy coatings on cracked surfaces. The lower part of the buff clay, as well as the pipe and fire clays, often contain 37 to 39 per cent. of alumina, and less than 1 per cent. of ferric oxide; while in the brick-clays the percentage of alumina is 17 to 21, and of ferric oxide, 4 to 6. Beneath the clay-beds stony ferruginous crusts and layers are sometimes observed, consisting of cemented sand or of cemented sand and clay. A process of alteration has also been reported[114] in the greensand deposits of New Jersey, as shown by the induration of barrel-shaped masses of green marl. While this is doubtless true, there are certainly other cases I have observed, as in the indurated greensand of the Navesink Highlands, in which the glauconite grains are found, on microscopic examination of thin sections, to be cemented by a very minute granular mass of the original calcareous organisms; in some specimens the foraminiferal forms are visible to the naked eye. It seems likely, therefore, that one effect of the solutions of humus-acids, continually percolating

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[112] Am. J. Sci., 1880, (3), XIX, 180.

[113] G. H. Cook. Report on Clays, 1878, 66, 85, 102-5, 195-239, 258.

[114] Rogers, Geol. of N. J., 1840, 197.

through this deposit, is to *dissolve out* its calcareous cement, as in the deep-sea ooze, afterwards described. The present loose uncompacted character of the greensand deposits may therefore, perhaps, be merely the result of such recent chemical solution and disintegration.

It has also been shown that the white Cretaceous clays, and the white fire-clays[115] and pipe-clays of the Coal-measures,[116] rich in alumina, and almost exhausted of iron and of the more soluble bases, as well as the gray sandstones and shales which always accompany the coal, demonstrate the leaching effect of the organic acids; the decoloration of the surface in red-clay soils, and the marbling of clay and bleaching along crevices, have been also assigned to the same cause. The white fire-clays of Pennsylvania enclose the marks of innumerable roots of stigmaria, etc., showing that they must have been crowded with vegetable remains.[117] I have also noticed that the clays in caves, as at Howe's Cave in Schoharie County, N. Y., are apt to show by their color, tenacity, etc., that they have experienced the same removal of iron oxide and concentration of alumina, by chemical action—probably of organic acids in the rain-waters which flood the cavities during and after storms.

VIII. ALTERATION OF FOSSILS.

§ 27. *Silicification of fossils.*—It may well be suspected that the silicification of calcareous fossils, presented on so large a scale in the Eocene buhrstones, may in some cases have been caused by organic acids, possibly derived from the decomposition of the associated lignites; and that such silicified strata may have been thus produced by an induration of antecedent sands or marls, as well as by the alteration of beds of solid limestones. It has been observed that lime and silicic acid frequently occur together as agents of petrifaction; siliceous crusts occur even in recent calcareous corals, and quartz-crystals are often found in the chambers of ammonites.[118] The silicification of wood, so abundant in Cretaceous and Tertiary deposits, may not always need for explanation the application of thermal solutions of silica, but rather that of this familiar but widely-distributed chemical agency, whose effect may in some cases have been even assisted and accelerated

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[115] Hunt, *op. cit.*, 13, 227.

[116] LeConte, El. of Geol., 136, 374.

[117] Rogers, Geol. of Pa., II, 737.

[118] Roth, *op. cit.*, I, 611.

by the high temperature of the waters. This subject is further considered beyond (§ 59).

§ 28. *Obliteration of fossils.*— Another result consists in the solution and obliteration of fossils, especially those of a calcareous nature, enclosed in porous masses of gravel, sand and clay, even when indurated. The absence of sea-shells from one such stratum, in Brazil, is stated to be "largely owing to the fact that they have been dissolved out by rains."[119]

Their general absence from extensive modern deposits, in South America, has been explained by the certainty of their disappearance from the surface by alluvial action and dissolution in rain-water.[120] In the Champlain deposits of this country, the scarcity of fossils is generally remarkable; they seem to be almost altogether confined to the blue clay,[121] which has been shown to be the remnant of the deposit but little affected by the acid waters infiltrating from above. It is even a question how far the marly character of most of these clays may be due to later and perhaps recent alteration, by such solvents, of former abundant enclosures of shells.

Again, the great Loess-deposit in this country, as also in Europe and China, is characterized by a significant absence of almost all fossils but those of a few terrestrial mollusks, *except where the material is clayey.* Richthofen, Pumpelly and Todd, have called attention to the abundance of fine tubular cavities, branching downward like root-marks, mostly confined to the upper portion of the Loess, being rare at a depth exceeding thirty or forty feet. The views of these observers, advanced on the still mooted problem of the origin of the Loess, have been partially founded on this absence of marine organisms; but Hilgard, in a recent paper,[122] suspects the connection of this absence from the mass of the deposit with the solution and re-deposition of calcium-carbonate, which at least he shows to be constantly and rapidly going on. Whether marine or terrestrial, vast numbers of shells appear to have been dissolved up, and their material often concentrated in the calcareous concretions which abound through the Loess. He made similar observations,[123] both on the scarcity of fossils and the associated abundance of calcareous concretions,

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[119] C. F. Hart, *op. cit.*, 82.

[120] C. Darwin, Geol. Obs., 1876, 415.

[121] Geol. of N. H., III, 165-166.

[122] Am. J. Sci., 1879, (3), XVIII, 108.

[123] Smith's Cont., No. 248, (1872).

in the deposits of the later Tertiary and overlying "Port Hudson Group" of the Southern States. In clayey layers the forms of shells were sometimes only partially obliterated; and there were transitions in the same stratum from an abundance of perfect shells, through all stages of obliteration, into a congeries of calcareous concretions in a more sandy and porous envelopment. The concretionary aggregation of these calcareous deposits points to the influence of organic acids of a colloid character, though, with calcareous fossils, carbon dioxide *may* suffice for their obliteration; with those which are siliceous, as in the chert pebbles of the Tertiary beds of New Jersey, acids of a more complex character, the azo-humic, *must* come into play.

The variety of changes through which fossils may pass, when replaced by so protean a material as oxide of iron, is also illustrated by the successive occupation of the cavities of a coral by limonite, siderite, and hematite, in the Northampton sands, England, with the final solution and entire removal of the coral itself.[124]

§ 29. *Formation of Concretions.*—The origin of calcareous clay-balls, argillaceous concretions, and septaria, is probably in large part connected with this process, and offers a promising field of investigation. The little that is now known, in regard to the development of these curious forms, has been chiefly derived from imperfect and ancient observations. Although the only organic acid they are known to contain is carbon dioxide, mainly combined with lime and in part with ferrous, magnesic, and manganous oxides, it may be merely the fixed residue of organic acids of more complex form, of which any remnant must be searched for mainly in the exterior layer or film. Even the subterranean decomposition of nitrogenous organic matters, such as seaweeds in marly clays, with a limited supply of oxygen, must have yielded other acids, besides carbon dioxide, to effect the concentration of the calcium-carbonate in the large nodular masses there observed.[125] Nor is it yet established even with siliceous concretions, such as those of Colorado, North Carolina, etc., whether the solvent has not in some cases consisted of solutions of humus instead of thermal waters.

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[124] J. Evans, Rep. Brit. Ass., 1878, 534.
[125] G. Forchhammer, Rep. Brit. Ass., 1844, XIV, 155.

IX. CHANGES WITHIN THE DEEP-SEA OOZE.

§ 30. *Evidences of chemical action.* — Recent discoveries by Wyville Thomson, Carpenter, and their coadjutors, have shown that chemical changes previously unsuspected, remarkable both in regard to character and extent, are in progress in the layer of ooze upon the bottom of all the oceans. There is a general and well-founded caution with regard to the reference of these changes to the agency of carbon dioxide; and I think that they can now be safely correlated with those carried on in sub-aërial strata, as already described, by organic acids, with the development of similar products. A brief review of the nature of these chemical changes will first be given.

The oozes over different areas, variously distributed and intermixed, consist of three materials: the first two of organic origin, *siliceous* and *calcareous*, according to the predominance of the siliceous organisms, *e. g.*, sponge-spicules, the diatoms, polycystines, radiolariæ, etc., or of the calcareous, *e. g.*, globigerinæ, orbulinæ, and other foraminifera: the last, the *ferruginous* or "red clay," in the deepest waters. According to Thomson the carbon dioxide of the sea-water has assisted in the production of a great part of the ferruginous ooze, by its decomposition of the calcareous shells of the foraminifera which live upon the surface, after their death, and by its entire solution and removal of their calcium-carbonate, during their long descent toward the bottom.[126] By this continual shower of the particles of the ultimate inorganic and ferruginous residue upon the bottom, he believes that the "globigerina-ooze" of the shallower waters passes into the "grey ooze," and, below the depth of 2500 fathoms, into the abyssal "red clay." Thus the amount of calcium-carbonate in the globigerina-ooze, forty-four to eighty-four per cent. by the analyses of J. S. Brazier[127] (61.3 by Hunter's analysis,[128] 58.8 by Mahony's,[129] and 50.1 by Forbes[130]), diminishes in the red globigerina-ooze, and still more in the red clay, ranging in these from 58 down to 1.5 per cent. The theory that the ooze-layer receives at least partial increments from deposits of this character is fortified by the experiment of Buchanan, who obtained nearly one per cent.

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[126] C. Wyville Thomson, Address before Brit. Assoc., Nature, 1878, XVIII, 450.

[127] Voy. of Chall., Atlantic, 1878, II, 315.

[128] Am. Chemist, 1870, I, 138.

[129] Chem. News, 1870, VI, 269.

[130] Depths of the Sea, 514.

of a red residue of similar composition to the "red clay," on treating a sample of globigerina-ooze with a dilute mineral acid. J. Murray states, "the most potent agent concerned in the removal of these shells from the majority of the deep-sea deposits is very likely that suggested by Prof. Wyville Thomson, viz., carbonic acid; yet there may be others." According to his view, however,[131] the genesis of the red clay has been due to the decomposition of feldspathic minerals, detected by the microscope in the ooze, which have been poured into the ocean in suspension by rivers and by atmospheric showers, viz., pumice, feldspar and sanidine, as well as augite, hornblende, quartz, leucite, magnetite, mica and olivine.

However, no experimental proof has yet been presented of the ability of carbon dioxide to overcome, in so short a time, the resistance to decomposition of the chitinous tissue of a recently living shell, and the protection from solution it affords to the enveloped calcium-carbonate. The known feeble influence of carbon dioxide upon the pumice, etc., especially under the conditions of temperature, etc., at the sea-bottom, renders it further probable that the chemical action has taken place *chiefly upon the bottom, within the ooze*, and at an inconceivably slow rate.

Again, nodules[132] have been found abundantly in the red clay, which consist mainly of manganic oxide, in part of ferric oxide. They are "round, oval, or mammillated, and very irregular, varying in size from a grain of mustard seed to a large potato." They possess a concentric structure, with a radiating fibrous arrangement, and "appear to form loose among the soft clay." The corals, otoliths, teeth, siliceous sponges, etc., which are often largely disseminated through this variety of ooze, frequently display a metasomatic alteration into the same concretionary material; and fragments of pumice or other minerals often constitute the nuclei.

Indications of flint,[133] of a somewhat indefinite nature, have been also frequently noticed, apparently occurring only where siliceous organisms were absent. Sometimes it was represented by a siliceous cement, binding together the shells of the ooze, in a gray flinty-like matrix; sometimes by small angular and soft pieces

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[131] Proc. Roy. Soc., 1876, XXIV, 531; Voy. of Chall. Atl., II, 253–255.

[132] Thomson and Murray, Proc. Roy. Soc., 1876, XXIV, 39, 464, etc.; Voy. of Chall., Atl., I, 169, 189, etc. Also in Loch Fyne, J. Y. Buchanan, Nature, 1878, XVIII, 628.

[133] Murray, *idem*, 491, 517, 524, etc.

of a cherty-like mineral; and sometimes by a yellow and green siliceous nucleus to the manganese nodules, occasionally presenting agate-bands.

In the bottom of the Pacific, the clay is sometimes found "in a peculiar concretionary state, run together into coherent lumps," or the blue mud has even experienced an induration into large pieces of rock, raised by the dredge, which are "merely hardened portions of the bottom."[134]

§ 31. *Organic matter in the ooze.*—Considerable evidence now exists that a substance corresponding to humus, simply in its yield of acid solvents of lime, oxides of iron, manganese, etc., enters universally into the constitution of the layer of ooze upon the bottom of the ocean. Its exact composition has never yet been determined; but it may be suspected that it resembles that of *glairine* (§ 20), especially in its high content of silica. As it has resulted from the continuous decomposition of the cellulose membranes of the diatomaceæ, etc., and of the gelatinous sarcode of the radiolaria, spongiæ, and foraminifera, which may be there living or deposited by subsidence from the surface, its composition must differ widely from that of the humus of subaërial eremacausis, in its large proportion of water and nitrogen and in its poverty in carbon. It must thus present the most favorable conditions for rapid dissociation.

Concerning the globigerina-ooze, it is said, "the stomachs of the more highly organized animals living in it or on its surface are always full of the fresher foraminiferal shells, from which they undoubtedly derive not only material for the calcification of their tests, but nitrogenous matter for assimilation likewise."[135] Indeed Ehrenberg found long ago that the foraminiferal shells at the bottom of the ocean are "not empty, but are often filled with organic substance;"[136] and a transparent gelatinous matter has been since observed by Huxley, and called *Bathybius*, in the form of innumerable minute lumps, scattered through the ooze, "forming a living scum or film on the sea-bed . . . . so that it probably forms one continuous scum of living matter girding the whole surface of the sea-bed:" and by Mahony, as particles still occupy-

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[134] Thomson and Murray, *idem*, 33, 499, 504, 506, 529, etc.
[135] Thomson, Voy. of Chall., Atl., II, 283.
[136] Bischof, *op. cit.*, III, 109.

ing the larger organisms, on the bottom at a depth of 2435 fathoms.[137]

In the diatom-ooze, there occurs especially an abundance of Holothuridea, often with their stomachs and intestines distended with the diatom-ooze, and, it is stated, "there can be little doubt that the diatoms sink to the bottom still retaining a small portion of their organic matter, which is slowly extracted by the alimentary canal of the Holothuridea."[138] In his analyses of the ooze of all varieties, Brazier determined the *loss on ignition*, after drying at 230° F., at from about four to ten per cent.; he also states, "the loss on ignition consists, for the most part, of water, probably water of hydration, but there is in all cases evidence of the existence of organic matter. The majority of the specimens, when treated with hydrochloric acid, evolved the peculiar tarry odor so characteristic of some of the limestones of this country."[139] Hunter's analysis of the ooze was evidently made upon material which had previously been both washed and ignited; but Forbes, in his analysis of Atlantic mud from the depth of 1443 fathoms,[140] obtains "*Organic matter* 4.19 *per cent.*," and J. Mahony, on the ooze from 2435 fathoms, obtains 2.30 per cent.

Thomson states, from a microscopical examination of the ooze dredged from the depth of nearly three miles, "the surface layer was found to consist chiefly of entire shells of *Globigerina bulloides*," together with fragments of these and other constituents of organic and inorganic origin, especially coccoliths and coccospheres, embedded in a viscous protoplasmic network. "Below the surface-layer, the sediment becomes gradually more compact, and a slight grey color, due, probably, to the decomposing organic matter, becomes more pronounced," the material gradually assuming a more fragmentary, finely-divided, and at last nearly structureless condition. Thus he states these shells are found "in the lower layers dead, and gradually crumbling down by the decomposition of their organic cement, and by the pressure of the layers above."[141] He then makes a comparison to a peat-bed, on the

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[137] T. Huxley, Quart. Jour. Mic. Soc., 1868, N. S., VIII, 205, and Proc. Roy. Geog. Soc., 1870, 38; J. Mahony, Chem. News, 1870, VI, 269.

[138] Thomson, *op. cit.*, II, 290.

[139] Brazier, Voy. of Chall., Atl., II, 325.

[140] Depths of the Sea, 514.

[141] Depths of the Sea, 410.

ground of these phenomena, which might be strengthened, in my opinion, by reference to the chemical reactions in progress.

§ 32. *Organic matter in sea-water.*— There is also much importance in the trace of dissolved organic matter which occurs in the waters of many seas, *e. g.*, the Baltic, Adriatic, Black, Caspian, Dead, etc.[142] The water of the Atlantic ocean itself contains substances allied to soluble humus, both in solution and suspension, which, according to Thomson,[143] probably serve for the nutrition of many forms of marine organisms, by absorption through their jelly-like bodies. In the composition of sea-water, as determined by the analyses of eight samples collected during the third cruise of the Porcupine, Dr. Frankland reports a "large amount of very highly nitrogenized organic matter contained in most of the samples," of which the amount may be represented, with a comparative reference to other waters, in the following brief summary of his results:[144]

Grammes in 100 *cc. of water.*

	Ocean.	River Thames.	Loch Katrine.
Organic carbon	0.00013 to 0.00065	0.00046	0.00016
Total combined Nitrogen	0.00017 to 0.00029	0.00028	0.00001

The vertical distribution of this substance bears a constant relation to the amount of animal life; and as the latter predominates in the zone near the surface of the sea and again in that upon the bottom, so the proportion of organic matter is less in the intermediate waters than above or below, and *most constant in the bottom waters.*[145] The sources of this substance can be assigned, not only to the continual decomposition of the organic portion of the ooze and of the dead bodies of marine animal organisms; but also, as pointed out by Thomson and Frankland, to the vast contributions of such material poured in from the land by all rivers—from the algæ along the shores, which occupy a band averaging a mile in width and sloping often to a depth of 100 fathoms—and to the vast marine tracts of seaweeds, such as the "Sargasso sea"

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[142] Roth, *op. cit.*, I, 469, 479, 525, etc.

[143] Depths of the Sea, 47; Proc. Roy. Soc., 1869, XVIII, June and Nov., 476, and 1875, XXIII, 238.

[144] Depths of the Sea, 511.

[145] W. L. Carpenter, *idem;* Buchanan, Proc. Roy. Soc., 1876, XXIV, 605.

in the Atlantic, with its 3,000,000 square miles of area. The enormous masses of decomposing vegetable matter in the salt-marshes, continually being leached along the margins of the oceans — in the submerged peatbeds, whose existence has been pointed out[146] along many shores — and in the organic portion of the dust of land-breezes, sweeping far out over the seas, represent other and important sources of this constituent of sea-water. One probable result of the further decomposition, by aeration, of the organic matter in the sea and in the ooze, is the development of carbon dioxide in a proportionate quantity in solution, which is much greater near the bottom of the sea, than at the surface: *e. g.*, by the average of the determinations of Buchanan,[147] 20.7 per cent. at the surface, 26.2 per cent. in the median zone, and 27.9 per cent. in the greatest depths. These bottom waters are therefore found to present the ocean-layer *richest in organic matter*, dissolved and suspended, *in carbon dioxide*, and *in calcium*, and *poorest in oxygen*, over the red-clay areas. Thomson has attributed this abnormal amount of carbon dioxide in the bottom-waters of the South Atlantic to their derivation from the surface-waters of Antarctic regions, in the course of the oceanic circulation; but all the characteristics just stated are exactly those consistent with contiguity to the decomposition of organic matter in the underlying ooze.

§ 33. *Presence of organic acids.*— From this point of view, there are the following reasons to suspect that other organic acids, besides carbon dioxide, may share to some extent in the submarine chemical action now attributed entirely to that gas. First, some of the humus-acids, especially humic and apocrenic, are certainly contributed by the rivers, decaying algæ, and subsided peat-beds and salt-marshes; and in the slow submarine decomposition of the sarcode of organisms, the development of other acids, possibly of this group, certainly of more complex constitution and even in nitrogenized combinations, probably precede and accompany that of carbon dioxide.

Secondly, the submarine concentration of manganese and iron

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[146] Along the shores of Great Britain, Lyell, Princ. of Geol., 1874, I, 548–550, and II, 536: around the Irish coast, Jukes, *op. cit.*, 686: at the mouth of the Pará, L. Agassiz, Jour. to Brazil, 1868, 434–5: at Ireland Island, Bermudas, Thomson, Voy. of Chall., Atlantic, I, 298: in the vicinity of New York, D. S. Martin, before N. Y. Acad. of Sci., Nov. 17, 1879, etc.

[147] Depths of the Sea, 498.

peroxides, in the concretions referred to, appears analogous to the exceedingly common sub-aërial process, resulting in the same products, which is certainly being carried on by the more complex acids.

Thirdly, the partial deoxidation and complete solution of the iron silicate out of the "red clay," and its deposition within and without the delicate structure of globigerina as perfect casts, in the form of glauconite, is an operation beyond the powers of carbon dioxide, and corresponds closely at least to the deoxidation and solution of ferrous oxide and silica by azo-humic acids in sub-aërial deposits. The problem, as yet unsolved, in regard to the origin of glauconite, may yet find a satisfactory explanation in this direction, when the exact character and action of the azo-humic acids shall have been more fully understood. Brazier found that the ignition of the ooze,[148] and Buchanan, that of the manganiferous concretions,[149] yielded water "with a strong alkaline reaction," "a property generally possessed by rocks and minerals;" and this property, as elsewhere shown in this paper, pretty certainly indicates always the formative work of the azo-humic acids and the remaining presence of a significant trace.

Again, the ultimate formation of nodules of flint in such deep-sea sediments, illustrated in its completion by the nodules and lenticular layers of that mineral and chert disseminated through all strata of Chalk and other calcareous formations, is generally explained by either of two theories: that the silica is concentrated from the amount existing in the waters of the ocean: or that the siliceous particles, contributed by sponge-spicules, diatoms, radiolaria, polycystines, xanthidia, etc., as well as those of inorganic character, fragmentary crystals, etc., are subsequently aggregated within the sediment: either process having been brought about by a mysterious entity represented by the term, "the force of segregation."

Since the studies of Leopold von Buch on the silicification of shells (Abh. d. K. Akad. d. Wiss., Berlin, 1828, 43) first called general attention to the remarkable way in which the deposit of silica has followed the extension of the organic substance of the animal, and that only, Bischof and most observers have recognized an important but as yet undetermined process of attraction between animal matter and silica. H. Johnson has suggested that

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[148] Voy. of Chall., Atl., II, 325.

[149] Proc. Roy. Soc., *loc. cit.*, 607–608.

the carbon of animal matter has been directly replaced by silicon; W. J. Sollas (Geol. Mag., 1873, X, 92) supposes that "when silicic acid is added to such animal matters as albumen or gelatin, it forms with them a definite chemical compound," from which it may be afterwards separated during decomposition. These theories require the introduction and addition of silica, necessarily from solution in the sea-water, to the organic matter in place. I would therefore modify Sollas' theory by suggesting that *during the decomposition* of the sarcode of both animal and vegetable organisms, after death, gelatinous or colloid substances are generated, resembling *glairine*, which are soluble in sea-water, which combine with silica and may therefore convey and concentrate it, dissolving its particles disseminated through submarine sediments, and which may in certain forms, produced by gradual oxidation, act also as acid solvents of lime, oxides of iron and manganese, etc. To this idea, in part, an early opinion of Bischof approaches: "silicifications are nothing else than the result of combinations between the crenic acids (quellsaüren) formed through decomposition of organic matter, *e. g.*, of mussels and oysters, and silica which, in aqueous solution, *e. g.*, as the water of springs, comes in contact therewith." (Erd. Jour. f. pr. Ch., 1834, II, 70–72.)

Now the globigerina-ooze has been found[150] to contain from about four to over twenty per cent. of silica, and the "red clay" up to 54.9 per cent., about half the quantity being in the soluble form. The established solubility of silica in solutions of the azohumic acids therefore suggests that, during the consolidation of the deep-sea sediment, such a solution of disseminated silica by albuminoids and by acids of this character is constantly in progress: that these solutions settle slowly into shallow basins, flow into fissures, and even percolate sluggishly below, along porous layers, generally perhaps submarine basins and subterranean layers in which organisms yielding siliceous particles may predominate: and that as the complex organic combination, probably resembling a lime-salt of a silico-azohumic acid, is dissociated by further oxidation, the dissolved silica is deposited in colloid condition over the surface of the basins, within the fissures, or below, along the drainage planes, around the undissolved siliceous organisms or particles as nuclei, or within the cavities of calcareous organisms during or subsequently to the removal of their calcium-

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[150] Buchanan, Voy. of Chall., Atlantic, II, 315–325.

carbonate. The amount of silica in solution in the sea-water seems entirely inadequate to account for such silicification, as suggested by some authors, nor is the process evident; while the frequent association of oxide of iron with silica, in such submarine replacements, appears to be an additional indication of the character of the solvents and process, as just described.

I find, therefore, the chemical reactions in progress within the submarine ooze-layer so similar in their results to those commonly observed in sub-aërial unconsolidated deposits (*e. g.*, the Tertiary and Cretaceous sands of New Jersey), that I am inclined to assign both to substantially the same solvent agency—that of *acids produced by organic decomposition.* There is but a single agency which on land is constantly producing the solution and concentration of ferric and manganic oxides, as well as of silica itself, and the cementation of sands by one or more of those three substances; a similar agent shows its presence and action by analogous results beneath the sea.

Only one material difference is apparent, that of the predominance of manganese over iron oxide in the concretions of the ooze, in that superficial layer within the reach of our investigation. The explanation is found, I think, in the *solvent action of sea-water*, as shown by its composition. In 1000 parts of sea-water, various analysts have found 0.0019 and 0.0022 ferrous carbonate in the North Atlantic Ocean, 0.005 in the Irish Sea, 0.0029 to 0.0065 in the Indian Ocean, etc.;[151] but *not even a trace of manganese* has yet been reported. May we not thence suppose, that, during the ages of the slow increment of the abyssal ooze, a constant solution and removal of the iron oxide has been carried on by the sea-water, out of the superficial layer, while the greater part of the manganese has merely been concentrated, peroxidized, and rendered insoluble?

ACTION UPON SOLID ROCKS.

§ 34. *Superficial decomposition.*—The *superficial* effects upon rocks of the corrosive action of acids, derived from decomposing vegetation, will not now be discussed. It is sufficient here to state my conviction that these effects, everywhere apparent upon naked surfaces of rocks, even when vertical, have been due, to a far larger extent than usually believed, to the initial and long

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[151] Roth, *op. cit.*, 505–531.

continued action of cryptogamous vegetation, especially that of the lichens and mosses; not so much perhaps by the direct action of the organic acids within the living tissues, as by those of the films or layers of humus underlying the encrusting sheets of these plants.

To these acids may be attributed also, to a greater or less degree, the excavation of shallow basins on horizontal surfaces, the loosening and separation of blocks of rock along the face of ledges, etc. At present we will proceed to consider the more profound effects of the same solvent agencies.

Even in those rocks in which alteration has been strongly resisted by their structure, *e. g.*, fine texture—by absence of lamination, fissures and cavities, *e. g.*, in many of the more compact eruptive rocks, possessing a glassy base—or by their chemical composition, such as the absence of soluble or unstable constituents, *e. g.*, the aluminous argillytes, siliceous sandstones, etc.—there is universal evidence of a deep and extensive decomposition. No quarry, mine, boring, or artificial excavation of any kind has yet been made to a depth which limits the progress of this alteration, at least along the most continuous and empty fissures. And wherever those minerals are abundant which are rich in soluble bases, *e. g.*, hornblende, chlorite, augite, etc., and particularly those which are unstable, *e. g.*, the metallic sulphides, there the decomposition is notoriously extensive, and affects and accelerates, by a kind of contact action, that of other constituents in which its progress would be otherwise slow. The waste material on the dumps of any mine presents a striking illustration of the rapidity of the last instance mentioned.

X. Erosion of Limestones.

§ 35. *General erosion and excavation.*—The ready solvency of limestone, even in carbon dioxide, has led to far more extensive and conspicuous results of erosion than those produced in most other rocks; and these have long been the subject of investigation by all geological observers. It has been pointed out that even "in the sea, vegetation carries on a slow degradation of the sides. Especially must it deeply corrode calcareous rocks."[152] Certainly, on the land, many of these results may be attributed in large part

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[152] M. Delesse, Lithologie du fond des mers, 1871.

to other organic acids, derived even from living vegetation. "We frequently find in meadows smooth limestones with their surfaces covered with a network of small furrows. When these stones are newly taken out of the ground, we find that each furrow corresponds to a rootlet, which appears as if it had eaten its way into the stone."[153]

The action of many acids, produced by decomposition, are surely concerned where bogs, rich soils, and similar accumulations of humus, rest directly upon a limestone-stratum. The general erosion this material has experienced,[154] in regions of abundant vegetation, is shown, even superficially, by deep pitting, gulleying, the removal of vast quantities of material, and, as Bischof long ago pointed out, the sinking of strata. The action has probably begun by the vertical sinking, both of a humus-bed and of its drainage-ways, into its easily soluble foundation, accelerating by the same process the work of mechanical corrosion. When an excessive amount of calcium-carbonate has been thus brought into solution—as when, in the tropics, a stream, overhung by dense vegetation, flows over coral rock—it may be constantly deposited upon the bed of the stream in the form of ridges and projections, enclosing basins.[155]

The joints and more irregular fissures which abound particularly in limestone-strata, have also been the seat of enormous erosion and widening into subterranean passages and caverns, chiefly by a chemical solution of their material, which has been mainly effected by carbon dioxide; though, during and immediately after heavy rains, the other humus-acids must have taken their part in this action. The excavation of caverns in the Sub-Carboniferous limestones, and the deposit within them of stalactitic limonite ores, "by the dissolving action of acid waters," "probably containing carbonic acid," has been largely discussed, for Missouri, by Dr. A. Schmidt and P. N. Moore (Geol. Surv. Missouri, 1872, 127, 640–1, and 1873–4, 405), and for Alabama, by E. A. Smith (Rep. Geol. Surv. Ala., 1879, 15).

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[153] J. Liebig, Modern Agric., 43.

[154] See the work of T. Mellard Reade on "Chemical denudation in relation to Geological Time," 1879. Also his paper on "Chemical Action in its geological aspect," Hardw. Sci. Goss., 1879, 6. The agency there considered is merely "the chemical action of rain."

[155] At Wokan Island in the Pacific, Mosely, *op. cit.*, 378; in Roaring river, Jamaica, De la Beche, Geol. Obs., 13.

Lesley has made careful study[156] of these caverns, in the Lower Silurian of Pennsylvania, with special reference to the following points: the support of the roof by the union of stalactites and stalagmites: the occupation of the caverns by clay, as a residue from the solution of the limestone: the metasomatic alteration of the stalactitic pillars into limonite (pipe-ore): and the letting down of the overlying beds and modification of the superficial topography.

The nature and extent of that alteration and of its significant product, limonite, suggest the associated action of other organic acids which are quicker and better solvents, both of calcium-carbonate and of ferric oxide, than carbon dioxide.

§ 36. *Extensive denudation.*—The most impressive illustration, however, of the vast power of these apparently feeble agencies, working quietly through long periods of time, is shown in the enormous denudation they have effected by chemical solution of calcareous strata over extensive areas.

Bischof gave the first full explanation of the results of this solution, in the formation of caverns and in the concentration of the comparatively insoluble impurities of limestones: *i. e.*, the production both of dolomytes,[157] by concentration of the feebly soluble magnesian constituents — of clays,[158] by the accumulation of siliceous residues — and of iron-ores,[159] by the concentration of iron-oxides. J. D. Whitney has observed, in the lead regions of Wisconsin,[160] a layer, averaging ten feet in thickness but sometimes reaching thirty feet, consisting of soil, sandy loam, and a red clay abounding in fragments of chert and galena or of undissolved limestone, resting upon a bed of that rock whose "surface is uneven and irregular, bearing the marks of chemical rather than of mechanical erosion." This layer Whitney considers to be the residuum left after the gradual solution, "by the simple agency of rain," of beds formerly extending over the whole region, some 350 to 400 feet in vertical thickness, of impure limestones, containing two to ten per cent. of insoluble matter and one or two per cent. of ferrous carbonate, as well as, in part, of cherty limestones and calcareous shales. The excavation of river valleys to a very considerable width and depth, throughout the same district, are considered attributable to the same agency.

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[156] Geol. Mag., New Series, 1879, VI, 459.

[157] *Op. cit.*, III, 180–202.

[158] *Idem*, 193–4.

[159] *Idem*, 337–340.

[160] Geol. of Wis., 1862, I, 117-126.

This process has been observed on a much larger scale among the dolomites of southern Missouri,[161] where it has produced, since the close of the Carboniferous period, "residuary deposits" of great economic importance, consisting of iron, lead, and zinc-ores.

Vast masses of a chert-breccia have been thus formed in Missouri, etc.; in Belgium also, near Dinant, etc., Dupont states that blocks of the "Pthanite" have been left, abundantly scattered upon the soil, by the more rapid solution and removal of the limestone (Bull. de l'Ac. roy. de Belge, (2), X, Nos. 9 and 10).

In England, Tertiary white clays have been observed, occupying pockets in the Carboniferous limestone (and elsewhere also derived from the Chalk), which contain the silica and alumina in the same proportions (2 to 1) as in the impurities of the limestone. It is therefore concluded that "they were left behind in the cavities after the calcareous matter had been removed by watery dissolutions" of carbon dioxide.[162] At Buxton, partially dissolved fragments of limestone occur beneath the thin covering of turf.[163] Argillaceous limestones, containing ferrous oxide, are thus often converted into "rotten stone" by the removal of calcium-carbonate, etc.[164] Similar examples occur abroad which I would refer to a corresponding concentration of the metallic oxides diffused through impure limestones. In the smithsonite and galenite deposits of the Muschelkalk formation of Upper Silesia and Poland, the following succession of beds commonly rests upon the dolomyte: 1, Surface soil — 2, Tertiary sand and clay — 3, Yellow Clay — 4, Limonite — 5, Clay — 6, White smithsonite, thirty inches to fourteen feet in thickness — and sometimes, 7, Galenite, in the dolomyte near smithsonite, or in pockets of the overlying beds. Beneath these, "the strata of the floor-limestone, which generally lie horizontally, frequently have their upper surface not parallel to the stratification, and *it appears as if eaten by acids*, so that fossils, and some harder ledges of the strata, are prominent."[165] Von Cotta recognizes a certain analogy between the formation of the limonite in the zinc-ore deposits and that of bog iron-ore. The formation of the zinc-ore he attributes to weak

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[161] R. Pumpelly, Geol. Surv. of Missouri, 1872, 9–13, and 1873, 8.

[162] G. Maw, Geol. Mag., 1867, IV, 420.

[163] "The waste of rock masses by solution," E. Brown, Geol. Mag., 1869, VI, 379.

[164] J. B. Jukes, Student's Man. of Geol., 1862, 158.

[165] Von Cotta, *op. cit.*, 248, 256.

zinc solutions re-acting on the dolomitic limestones; but the very analogy to bog-ores, referred to, seems to indicate that the solution of the zinc-oxide itself has been caused as well by the action of one or more of the same organic acids.

Besides this action of denudation, it has even been suggested that the metamorphism of sedimentary limestones into the crystalline condition has been, in Brazil, produced "by soaking with meteoric waters."[166]

It has also been noted that a decoloration, produced by the same agency, has affected the gray and yellow dolomytes and limestones of the upper Silurian in Livonia, etc.[167]

XI. POROUS SEDIMENTARY ROCKS.

§ 37. *Saturation of porous masses.*—In the examples of decomposition just discussed, reference has been made only to those rocks whose density is so great as to resist the passage of waters, to any considerable extent, except through fissures or along those porous planes of stratification in which the constituent grains are aggregated more loosely or by a more soluble cement. But enormous masses of rock occur, chiefly sedimentary, whose material is itself decidedly porous and has afforded opportunity for considerable movement of infiltrating waters through the mass as well as through its division planes. In this connection there is great importance in the experiments of Barry, Delabeche, Smith in 1839, and later D. T. Ansted,[168] T. S. Hunt,[169] and C. Lang,[170] on the porosity of rocks. The calculations of Ansted and Hunt on the vast quantities of liquid which can be held in the pores of all common sedimentary rocks, have a new and special application to their frequent actual content of, and perhaps occasional saturation by weak solutions of the organic acids, during elevation above the sea-level.

An excellent illustration of the results of such a saturation of a porous mass is shown in the sedimentary sandstones. In these, however, the influence of organic acids is shown in two ways, which need to be clearly distinguished. First, in the degree of the purification of their original materials, before consolidation,

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[166] C. F. Hartt, Geol. of Brazil, 280.

[167] Schrenk, Arch. f. naturk. Liv., etc., (1), I, 24.

[168] Chem. News, 1860, II, 223.

[169] Essays, 104, 164.

[170] Zeitschr. f. Biol., 1876, XI, 313–340.

from all soluble and decomposable substances; this has been already partially considered, in reference to the beach-sand deposits of the present Atlantic coast, and is further discussed in the historical review in the closing section of this paper. Secondly, in the solution, transport, and frequent concentration of their interstitial matters by meteoric waters infiltrating downward from the present land-surface. The principal sandstone formations will now be considered in historical order, with reference merely to this latter method of chemical alteration.

The dunyte-beds of North Carolina, which I regard merely as slightly altered sediments — as it were, metamorphic sandstones — made up chiefly of olivine grains, have presented, by their ferrous constituent, a material accessible to an extensive decomposition which will be hereafter described.

§ 38. *Silurian sandstones.*— When almost entirely siliceous, both in their grains and their cement, like those of the Silurian, there was little opportunity for decomposition, except in the few scattered grains of feldspar. The only results are comprised in the kaolinic cementation of certain layers, the concentration of ochreous deposits in others, the decoloration of the more quartzose and porous layers, the general dissemination of more or less opaline silica in the form of cement, and the consequent mottling of the rock in cross-section by irregular stripes and spots of red and white. All these forms of recent decomposition are well shown in the Potsdam sandstones of northern New York, the lithologically similar sandstones of the pre-Silurian tract along the southern shores of Lake Superior, the finer grained grits of the Shawangunk conglomerate which caps the ridge of the mountain of that name in New York, and the similar grits of Lookout Mountain in Tennessee.

The St. Peter's sandstone of Wisconsin exhibits a remarkably mottled coloration in brown and white, and the ferric oxide is often so concentrated that "in the upper part of the formation, irregular concretions of iron-ore occur;" and in some places the ochres of this sandstone are separated by crushing and washing for paint.[171]

In Minnesota, the rock appears to have been originally a purely siliceous sand, very feebly cemented; and its present

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[171] T. C. Chamberlin and M. Strong, Geol. of Wis., 1873–77, II, 286, 723.

ferruginous bands and mottling appear to have been subsequently produced by local percolation of ferruginous solutions.[172]

The "Pictured Rocks," of the sandstones along the southern shores of Lake Superior, also present a familiar illustration of lateral exudations, produced by this form of chemical action.

§ 39. *Devonian Sandstones.*—The Devonian sandstones and flags, as represented in the interior of New York, I find to consist chiefly of angular to sub-angular grains of quartz and feldspar, with their interstices occupied by smaller grains of magnetite, scales of chlorite, and particularly short fibres of hornblende interlacing the grains of the other constituents. The result is an "argillaceous sandstone," flagstone, or greywacke, peculiarly compact and impermeable, which has retained its fresh condition to an extent which could not otherwise have been expected from an aggregate of substances so liable to ready decomposition. Nevertheless the impure greenish sandstones of this character which form the bulk of the Catskill Mountains, notwithstanding their general fine texture and density, display a decomposition of the mass and oxidation to a brownish tinge, sometimes to the depth of over two feet.

In England, Young[173] has found the cement of the Old Red Sandstones to contain from six to twenty-six per cent. of calcium-carbonate; and it would seem probable that such a calcareous cement, common both in the Devonian and Carboniferous sandstones, may have been derived, at least in part, from infiltration from overlying limestones or from the decomposition of enclosed silicates, in either case partly effected by percolating solutions of the humus-acids.

§ 40. *Carboniferous Sandstones.*—The cream-colored sandstones of the Sub-Carboniferous, largely quarried as a building stone and exported from Nova Scotia, contain, in addition to quartz, a considerable amount of the feldspars in small angular grains, kaolin, iron-ochre and a little chlorite in minute scales. The more readily decomposed constituents, which in general can be distinguished only on a microscopical examination of thin sections of the rock, are effectually protected from attack by meteoric waters, in part through their fine grain and close aggregation, but chiefly through the kaolinic powder which completely fills up their interstices with

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[172] N. H. Winchell, Geol. and Nat. Hist. Surv. Minn., 1876, 146.

[173] J. Wallace Young, Chem. News, 1868, III, 307.

a compact almost impervious cement. To this are due the fresh condition and almost uniform cream-color of the quarried rock, as well as its excellent and long continued resistance, when exposed to the weather, to decomposition and discoloration.

The ferruginous sandstones of the Carboniferous may be included in the discussion, below, of their lithological equivalents of later age.

§ 41. *Mesozoic Sandstones.*—A microscopical and chemical examination of the brown freestone from Portland, Connecticut, reveals the following components: quartz, largely predominating in clear sub-angular grains: orthoclase, muscovite, and ochreous ferric hydrate:[174] occasional particles of plagioclase, hornblende and magnetite, and scales of chlorite: and a constant though very small amount of amorphous calcium-carbonate.

Near the plane of contact with the overflows of diabase, which form a conspicuous feature in this horizon, in the form of the well-known trap-dykes of Connecticut, New Jersey, etc., the metamorphism has been so general and profound that often, though not always, the contiguous layer of sandstone, to the depth of five to ten feet, has been converted into an indurated arkose, black "trappean schists," or an actual feldspathic quartzyte, in which the cement often consists of opaline silica, as shown by careful analyses.[175] Such compact varieties of course have experienced little decomposition except superficial and kaolinic, by the passage of meteoric waters. But the predominant variety of this rock, that which is extensively exposed in the quarries of Connecticut and New Jersey, affords, I think, unmistakable evidence, in many strata, of the passage of percolating solutions of aerated and carbonated waters, and probably of the acids of organic decay, attended by the attack and partial decomposition of certain constituents of the rock. The nature of the decomposition is shown, in the thin sections, especially by the grains and scales of chlorite, biotite, hornblende, etc., in all stages of ochreous alteration; and to this may be *partially* attributed the abundance of reddish ochre which fills up all interstices. The chlorite is probably prochlorite, a mineral which, as already shown in Bolton's

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[174] Cook reports three per cent. of ferric oxide and four per cent. of alumina in one specimen examined (Rep. Geol. N. J., 1863, 509).

[175] H. Wurtz, Proc. N. Y. Lyc. Nat. Hist., 1870, 99–105. P. Schweitzer, Am. Chem., 1871, July.

table (§2), is readily decomposed in the cold by the action of citric acid.

§ 42. *Decomposition of organic remains.*—The subterranean oxidation and decomposition of vegetable remains, within strata of all formations, is also an important mode for the internal development of organic acids. Illustrations of this fact are abundant and well known. Prof. D. S. Martin has observed, at Newark, N. J., masses of Triassic sandstone, in which vegetable remains plentifully occur, bleached to greenish-yellow and light-gray. A similar reduction and change of color in large masses of the rock have been observed by Profs. H. C. Bolton and A. H. Chester, in the quarries at Portland, Connecticut; the Silurian sandstones along the shores of Lake Superior are often peculiarly spotted and mottled in this way; and in many of these cases nuclei of organic matter may be detected near the centre of the lens or sphere of bleached rock. The same fact is of common occurrence in the layers of the Devonian and Carboniferous sandstones which contain carbonized plants, fishes, etc., in central New York and elsewhere. In such cases the solvent action of organic acids is probably in progress, such as the carbo-ulmic and carbo-humic acids of Herz (*vide ante*), derived from lignite; in fact, Reichel has reported both bituminous resin and ulmic acid, in his analysis of the cement of a sandstone from Saxony.[176]

All loosely aggregated and porous sandstones exhibit the same results from infiltrating acid solutions.

The Triassic sandstones largely quarried in the vicinity of Heidelberg, in Baden, I found to display the same concentration of iron-ochre, often to a degree not usual in American localities, in large bunches which were sometimes almost pure limonite-ochre; a similar concentration of iron-oxide in streaks, powder, etc., has been observed in the Carboniferous sandstones of Missouri (Geol. Missouri, 1873, 42).

Action upon Slates.

§ 43. *General softening.*—From the chemical composition of argillytes and other crypto-crystalline schists, they have offered a remarkable resistance to the chemical action which has caused the decay of other rocks. Of course this resistance has been prob-

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[176] Bischof, *op. cit.*, III, 99.

ably due in large part to their fine texture and impermeability. The decomposition effected is ordinarily shown by a softening to a pulverulent clayey mass, still retaining the schistose structure, and an oxidation of protoxides, indicated by the passage of the hard blue and green argillytes into softer clay slates and shales. Familiar examples of this disintegrating action occur on all slate-terranes, *e. g.*, in this country, in Vermont, North Carolina, the Huronian areas of Michigan, Wisconsin and Canada; and its comparatively shallow depth, rarely over ten or fifteen feet, has often enabled these soft rocks to project in ridges and swells, in defiance both of glacial excavation and recent erosion.

In many cases, also, the green mottling of the hard blue roofing-slates appears to be one of the deeper-seated later effects, of secondary origin, brought about by an alteration of the condition of oxidation of the iron-oxides by percolating acid solutions.

§ 44. *Red Shales.*—Again, there is some reason to believe that the rock of the Catskill formation, in the Catskill mountains of New York, styled the "red shale," should more properly be called the "green shale." The original color and condition of oxidation, still retained in the underlying mass, seemed to me to be occasionally revealed in fresh excavations by streams or artificial means, at many points in the vicinity of the Kaaterskill Clove, and even along the road on the ascent to the Mountain House. The term generally accepted seems to be an instance of the erroneous conclusions and names which have been often founded upon the visible characteristics of the superficial and decomposed crust of a rock; in fact in many regions, the true lithological character of certain strata, entirely unaffected by decomposition, has never yet been seen, or perhaps only in artificial shafts of extreme depth.

The deposit of red clay which deep-sea exploration has revealed over the ocean bottom off the coast of South America, and which the naturalists of the Challenger attribute to the silt of the large rivers of that continent, illustrates the conditions of the formation of the red silt, containing the iron in peroxidized state, which constitutes the coloring material of Triassic sandstones and red shales. But, in general, sufficient organic matter has been intermingled with such silt deposits to reduce most of their free iron-oxide, very soon after consolidation, to the ferrous state. And in the Catskill formation, a comparatively impermeable cap has been supplied, for protection from later alteration, by the conglomerates and remarkably compact flags which overlie and are interbedded with the shales. In the flags, the oxide of iron of the detrital ingredients is largely in a ferrous condition, and the rock is green, which is everywhere apparent because the "weathering" has penetrated but one or two feet into the compact material. This alone would create a presumption that the finer sediments, now represented by the shales, must have been originally of the same character and color; and their thin lamination has caused the shales to be affected by a deeper decomposition (often fifteen or twenty feet) than the more compact associated flags. Again, in the red crust of these green shales, a subsequent return of the iron to the ferrous condition is often shown, in the Catskills, by a green veining and mottling, sometimes of an extensive character, in strong contrast with the red color of the shale. On close examination it is always found to be connected with or intersected by the natural joints and fissures of the rock, and may be certainly attributed to the reducing effect of solutions of organic acids, percolating through the joints from the rich humus-layer which clothes the sides of the mountains. This green variety of shale of recent origin seems in general to be easily distinguished from the green color of the unaltered underlying rock by the peculiar brightness and shade of the green color.

A similar alteration has been noticed in some of the hematitic phyllytes of Belgium, which carry the layers of garnetiferous honestone (coticule).[177] The margins both of the natural cleavage-joints and irregular fissures are softened and bleached to a yellowish-white color, to the width of several millimeters up to one centimeter. The action has been attributed to "atmospheric agents" in percolating waters, washing the carbonaceous coloring particles out of the slate and converting the hematite into limonite. Reference may here be made to the spotting, often regular and producing a beautiful effect, which is sometimes seen, both in red shales (as at the "Red Chasm" in the Kaaterskill Clove), and in the green slates of Vermont and the green Cambrian slates of Wales.[178] This seems to originate from nuclei, sometimes of or-

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[177] A. Renard, Mém. sur le struct. et la comp. min. du coticule, 1877, 39, note.

[178] G. Maw, Geol. Mag., 1869, VI, 576.

ganic matter but sometimes of pyrite, and may not always have connection with the organic agents now under discussion.

XIII. Disintegration of Crystalline Rocks.

§ 45. *Deep decomposition.*—It is a fact of universal observation that crystalline rocks in place, whose denuded surfaces are covered with a weathering crust, rarely exceeding two or three inches in thickness, present internal evidences of decomposition to a great depth, in some cases even several hundred feet. The seams of stratification, slaty lamination, joints and irregular fissures, are lined or nearly filled with ochreous and generally pulverulent deposits of the hydrates of the various higher oxides of iron and manganese. Within ten to fifty feet of the surface, even those rocks, which at first glance appear compact and fresh, reveal on closer examination, astonishing evidences of their permeability and of the corrosive agency of infiltrating meteoric waters. Perhaps that class of rocks, both crystalline and sedimentary, in which orthoclase is a common constituent, and which cover a large extent of the earth's surface, presents the most conspicuous illustration, on the one hand, of apparent compactness, impermeability, and apparently favorable conditions for resistance to decomposition, and, on the other, of the indubitable evidences of profound and often extensive change. For example, the Montalban gneisses of even our northern states present these evidences in a remarkable degree. In an ordinary specimen of the micaceous gneiss, poor in feldspar, abundant on New York island, taken from a depth of about ten feet and apparently but slightly altered, on a section across the lamination from ten to twelve ochreous seams were counted to the inch, each covered by a mere film of the reddish ferric hydrate, but so thin and inconspicuous, as to be hardly visible except where the fracture ran obliquely across. On digesting the powdered rock in dilute hydrochloric acid, I was surprised to find that it yielded 7.71 per cent. of ferric oxide; so that taking five per cent. as the average, in every 100 cubic metres (130 cubic yards) of this rock the amount of 13.5 metric tons (13.2 English long tons) of ferric oxide, or 9.45 metric tons (9.3 English long tons) of metallic iron, is on its way to lower drainage-levels: either to pass into the river and bay, and so into the ocean, or, as the conditions of the topography shall determine, to be arrested in some glacial rock-basin and marsh, in the form of beds of bog iron-ore, usually manganiferous. And large beds of this ore were found in abundance in the bottoms of the valleys, on the first settlement of Manhattan island.[179]

§ 46. *Various theories.*—The disintegration of granyte (maladie du granit) has long ago been considered by Dolomieu and attributed by him to the action of carbon-dioxide evolved from subterranean vents. Darwin[180] first called attention in 1851 to the remarkable extent of this decomposition, as shown in Brazil, but suspected that it had taken place during submergence beneath the sea. Heusser and Claraz suggested[181] that the agent was "the dissolving action of water, which increases with the temperature," aided by some nitric acid derived from the atmosphere. Agassiz[182] considered that the disintegration of rocks in the tropics had been effected by "the warm rains falling upon the heated soil." T. Sterry Hunt[183] called attention to the depth and extent of this disintegration, in all the crystalline schists of the southern United States and of Brazil, and assigned its cause to the influence of "the peculiar composition of the atmosphere, in early times," especially when rich in carbon-dioxide during the Carboniferous period. Hartt, in his careful study of the phenomena in Brazil,[184] assigns the cause to warm rain-water, carrying carbon-dioxide both from the air and from vegetation decaying upon the soil, "together with organic acids, nitrate of ammonia, etc." He also states his belief that the alteration occurs only in regions anciently or at present covered by forest. Further observations have been contributed by J. D. Dana on the Pacific islands and South American coast,[185] Pumpelly in China,[186] Missouri,[187] etc., L. S. Burbank in North Carolina,[188] Dr. Benza in Hindostan,[189] Le Conte on the general subject,[190] and many others. I hope hereafter to present a further discussion of the phenomena as exhibited in North Carolina. It is sufficient for my

[179] Mather, Nat. Hist. of N. Y., 1843, IV, I, 120.
[180] Geol. Obs.. Ed. of 1876, 427–8.
[181] Ann. d. mines, (5), Mém., 1870, XVII, 291.
[182] Letter of 1865. Jour. to Brazil, 1868, 86–89.
[183] Chem. and Geol. Ess., 1871–1873, 2, 10. 20, 41, 101–3, 250.
[184] Geol. and Phys. Geog. of Brazil, 1870, 24.
[185] U. S. Expl. Exp., Geol., 1846–9, 298, 513, etc.
[186] Smiths. Inst., 1866, 72, 73, 26.
[187] Geol. Surv. of Missouri, 1873, 8.
[188] Proc. Boston Soc. Nat. Hist., 1873, XVI, Nov.
[189] Madras Jour. of Lit., 1836, 246.
[190] El. of Geol., 4.

present purpose to state that this action may be attributed simply to the effect of the abundant vegetation which formerly clothed the surface of that state, and which probably rested, as it now does in the mountains of the western part, upon a thick and rich black layer of decomposing humus. So that, both in Brazil and in our southern states, the main agents of disintegration have been mainly derived, I believe, from neither atmospheric nor subterranean sources, but from the heavy primeval forest-growth which preceded the inroads of our present civilization. And of these agents carbon dioxide has been but a single, and, in the *superficial* work of chemical erosion, a subordinate member.

In the satisfactory hypothesis, recently advanced,[191] in regard to the secular rock-disintegration which preceded the excavation of rock-basins by wind, water, or ice, especially in post-Tertiary times, attention was called to the relationship of the character and degree of the alteration to the chemical composition of the material of the rock itself: the property of resistance to carbon dioxide having determined the survival of a mass, rather than the property of hardness which chiefly controls the extent of mechanical erosion. If, however, in addition to the "carbonic acid, water, and free oxygen" to which the author refers the disintegration, the agency of complex organic acids, having a solvency for silica, has been concerned, as now suggested, it might be expected that an alteration by such agents will be shown by a depth and character of products depending upon the solvency, and ready susceptibility to chemical decomposition, of the *silicates* of the crystalline rocks. This will depend therefore not entirely, often not even chiefly, upon the action of carbon dioxide, and can affect not merely the feldspars, but, as we actually find, all silicates without exception. The degree of the decomposition, however, varies greatly with the chemical nature of the rock: so that, as Pumpelly has pointed out, glacial action has been compelled to spare projecting ridges of even such materials as the soft clay slates and mica schists.

Prof. W. C. Kerr has verbally described an interesting example in North Carolina, with which I have also been impressed, of the remarkable contrast between the deep decay and disintegration of the crystalline rocks of the "Greensboro belt," *e. g.*, gneisses, diorytes, greenstones, etc., stretching across the state from north-

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[191] R. Pumpelly, Am. J. Sci., (3), 1879, XVII, 133.

east to southwest, and the thinly disintegrated or even almost naked surface of the aluminous slates of the parallel belt on the east; though even in the latter a decomposition to a great depth is usually shown by their alteration from hard blue or green argillytes to softened and ferruginous clay slates.

XIV. Theory of Subterranean Decomposition.

§ 47. *Principal agents.*— What has been the agency to which we must attribute the decomposition of minerals, as well as the transport of their products, in such enormous quantities? We can not look upon carbon dioxide solely, and, it is probable, not even chiefly, as the *attacking agent:* though it may have served as the main *vehicle for transport* of the decomposition products. It can not even dissolve the iron-oxide, except in the ferrous condition; soluble humus-substances, it may be in the simplest forms, ordinarily called "amorphous," must serve for the previous deoxidation of ferrous silicates; this very process is synonymous with the oxidation of the organic matter to the more complex forms, which are the acids mainly under discussion, and still exert strong reducing power; and finally, these acids possess far greater efficiency for corrosive attack than carbon dioxide, in their far greater solvency of all the iron-oxides and other bases, as well as of the silica therewith associated.

Messrs. W. B. and R. E. Rogers have shown (Am. J. Sci., 1848, (2), V, 401), in a brief statement of their experiments on a series of about thirty-six minerals and rocks, that carbonated or even simple water exerts an appreciable effect in their decomposition; and that, with the magnesian and calcareo-magnesian silicates, *e. g.*, hornblende, chlorite, etc., an amount of 0.4 to 1 per cent. may pass into solution, by prolonged digestion in carbonated water. On these grounds the natural solutions of "carbonic acid, water, and free oxygen," have been the agents invoked by Ebelmen, Detmer,[192] Boussingault,[193] Pumpelly, and most authors, to account for the forms of enormous chemical erosion, just described. However, the more definite experiments of Beyer[194] have an important significance, in opposition to this conclusion. On treating one kilogramme of finely-ground feldspar with two and one-half

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[192] *Loc. cit.*, 249.

[193] *Loc. cit.*, 397.

[194] Dr. A. Beyer, Die Landw. Vers. Stat., 1871, XIV, 314–322.

litres of water and of various saline solutions, during about twenty-nine months, he obtained results of which it is sufficient here to quote the extremes. The amount, in grammes, of the constituents of the feldspar found dissolved in each solution, was as follows: —

Distilled water	0.29,	solution of gypsum	4.92,
aerated water	0.19,	solution of magnesia and carbon dioxide	8.29.
carbonated water	0.39,		

He therefore concludes that carbon dioxide and aerated water have exerted, during this period of the experiment, no essential effect.

The conditions of the process of subterranean decomposition of rocks, by the humus-acids, now in progress, therefore appear to be intermittent, and to depend upon the character and thickness of the superincumbent layer of soil: upon the climate and season of the year, as determining the amount of rainfall, the temperature of the soil and of the meteoric solutions, and the nature and extent of the process of eremacausis in the humus: and upon the abundance, width, slope, extent, amount of obstruction, freedom of drainage, and duration of dryness, in the capillary fissures, pores, or wider cavities in the subjacent mass of rock.

§ 48. *Three zones.*—In the ordinary conditions of those strata, under our observation, which are elevated above the sea-level and freely drained, three vertical zones of chemical action, produced largely through these acids, may be distinguished.

The highest zone, next to the surface, is constantly subjected to the action of all the acids of humus, as well as atmospheric waters; and in this the most extensive and continuous process of corrosion and solution is going on. It is probable that its depth in our climate, during the summer, rarely exceeds ten to twenty feet, but must be actually very variable, ranging from a few inches, during excessive droughts, to at least hundreds of feet, during long continued rains. And with the heavy rains of autumn, the continuous saturation of the subterranean strata during the winter, and the thawing of snows, the floods, and the frequent showers of spring, a large part of the soluble matters of humus must be leached out of the soil, to find its way in part and to extend the process of corrosion of the rock and transport of its soluble constituents to still more profound depths.

Next below comes a median zone, into which, during an ordinary summer season, the more complex organic acids can rarely penetrate and in very minute quantities. As they infiltrate downward after a rain, the oozing solution of organic salts of iron, manganese, etc., becomes more and more mixed and saturated with the air which occupies the pores and fissures of the rock; the more complex humus-acids become oxidized to simpler forms; all the silica and the larger portion of the iron, manganese, and other bases, are deposited; most of the ammonia is evolved, locked up in clays, or returned to the surface; and a portion of the iron continues on its downward way as ferrous carbonate, in company with the more soluble carbonates of lime, magnesia, and the alkalies. The limits of this zone, as just explained, are trenched upon or completely included by the upper, through the downward moving floods after the heavy rains of summer and in the course of the rainy season. It is only during the latter that the corrosive action can exert much influence; and during other and ordinary seasons this zone must be chiefly the highway of transport of the products of decomposition of the superficial strata, of their frequent oxidation and deposit, and of their repeated though intermittent re-solution, in the simplest forms, and conveyance to a horizon still more profound.

In the lowest zone of all, the process of corrosion must be exceedingly slow and intermittent, and merging gradually into the metamorphic processes developed by the increasing subterranean temperature. Only the carbonates of the bases are brought down in solution, especially those of the alkalies, and take their important part in the process of metamorphic alteration; while the more complex acids of humus rarely penetrate to so great a depth, and have there merely an ephemeral action and duration.

XV. ACTION WITHIN VEINS.

§ 49. *Formation of Gossan.*—The depressions of the surface of the ground, along the course of a vein or elevated bed of soft or erodable ore, have generally invited the gathering of surface waters, the formation of swamps, rich in humus, and the consequent concentration of solutions of its acids. The steep inclinations of the crevices, especially along the planes of contact with the strata traversed, have allowed these solutions to penetrate to enormous depths. The gossan, whose formation as a cap to the vein must be largely due to these erosive agents, does not exceed fifty or sixty feet in depth according to the books, but apparently reaches at least 200 to 300 feet in many of the Western mines, sunken on well-drained fissure-veins; and the ochreous selvage along the walls, and scattered films and bunches along the more continuous and dry fissures, certainly reach to a still greater depth, *e. g.*, 1500 feet in the Eureka mine, in northern Nevada.[195] The material of the gossan has certainly been the seat of a most complex series of chemical reactions, perhaps unsurpassed elsewhere in nature; and in these the acids of humus have played a very important part. This seems to be indicated by the remarkable decomposition and softening of the wall-rock and of refractory sulphides, the deposition of limonite and hyalite, the evidences of strong reduction, as well as intermittent oxidation, the separation of the native metals (copper, silver, gold, etc.) in forms which must have required a strong reducing agent and solvent, the abundance of carbonates and even of combinations of other humus-acids with oxide of iron, etc. The enclosure of brown iron-ore in gold nuggets, the intimate and almost universal intermixture of the brown limonite with minute shot gold, at depths of even 100 feet in mines of North Carolina, as well as the abundant association of gold with the ferruginous conglomerate (Jacotinga) of Brazil, etc., seem to indicate a different agency, perhaps of solution, than that of the inorganic mineral solutions which usually also traverse veins and beds.

Although the deep gossan, heavy *limonitic deposits*, and still deeper decomposition, which are connected with the veins of metallic sulphides, chlorides, tellurides, etc., in the arid and barren plateaus of Nevada, Colorado, Arizona, etc., have been naturally referred to by Dr. Newberry as affected by a "dry rot," I believe that the chemical action and products, there represented, afford indubitable evidence of the existence of abundant moisture and vegetation, and of an extensive humus-layer, during some antecedent period. This seems to be confirmed by the close parallel exhibited upon the South American continent, where the enormous superficial sheets of limonite, shot-ore, and even the ferruginous Tertiary sandstones, of Brazil, now underlying dry plateaus, almost destitute of vegetation, have been certainly derived, according to such observers as L. Agassiz, Hartt, and Dr. R. P. Stevens of

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[195] Dr. J. S. Newberry, before N. Y. Acad. Sci., 1880.

New York, from the decomposition of thick strata of the crystalline rocks, and concentration of their iron-oxide, by organic acids, etc., washed down from an ancient humus-layer of the then forest-clad uplands.

§ 50. *Relationship of ores.*— Bischof has called special attention[196] to the intimate connection prevailing in nature between gold and iron (the latter either as sulphide or oxide), and also between quartz and gold; it is a suggestive fact that the strongest solvents in nature of these associates of gold, iron-oxide and silica, are the humus-acids. The *precipitation* of gold and of auriferous pyrites in many "placer" and vein deposits, within the interstices of lignite, in diffusion through clays, ochreous gossan, etc., indicates the reducing efficiency of "organic matter"[197] in its most soluble and probably therefore, in part, its acid forms, in a most important class of deposits. The formation of the diamond, and similar problems, may yet receive light from a better knowledge of these organic acids and of their solutions occurring in nature. When the significant association of this mineral with *limonite*, in the Urals, and in the ferruginous conglomerate of Minas Geraes in Brazil, is considered with reference to one of the common theories of its origin, that of Bischof, "the reciprocal action of peroxide of iron and decaying organic matter,"[198] the facts suggest at once the possible intervention of some of the organic acids and iron-salts already considered.

Numerous examples of the deposition of metallic sulphides and of native metals by "organic material" are on record, which partly pertain to the action of the organic acids.

Senft finds by experiment,[199] that through the action of the humus solutions, silver-chloride becomes soluble, that the zeolites and simple feldspars dissolve more or less, and that even compound silicates (*e. g.*, oligoclase, mica, ordinary hornblende, and augite) are at least partly decomposed. His later experiments[200] have shown him a great difference in the solvent power of the agencies — the ammoniacal and other alkaline combinations of the humus-acids — which he believes most efficient in the decomposi-

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[196] *Op. cit.*, III, 534.

[197] C. Newberry, Am. Jour. Min., 1868, Sept. 12; R. W. Raymond, Mining Res. W. of Rocky Mts., 1870, 449; A. Murray, *idem*, 1871, 508.

[198] *Op. cit.*, I, 250–1.

[199] Zeits. D. geol. Gesells., 1871, XXIII, 665.

[200] *Loc. cit.*, 1874, XXVI, 954.

tion, alteration, and transport of mineral substances. This power is least in the ulmates, which can dissolve only carbonates: it is stronger in the humates, which dissolve both carbonates and phosphates: and it is strongest in the crenates, especially that of ammonia, which dissolve carbonates, phosphates, sulphates, simple silicates, and fluorides. The salts thus dissolved remain in solution only in inverse proportion to the degree of their subsequent conversion into carbonates: the latter separating, in crystalline condition, in proportion to their insolubility in carbonated waters. The arsenides of nickel, of cobalt, and of iron, and the sulphides of iron and of lead, reduce salts of the heavy metals in solution in humus-acids, and deposit the metals of the latter in close contact, by a process attended with galvanic action. These observations throw light upon the formation of certain minerals in veins, and the occurrence of pure native metals in close envelopment about the arsenides and sulphides above mentioned.

When the walls of a vein are composed of a very soluble material, like the limestone-strata which enclose the ore-deposits of Illinois, Wisconsin and Missouri, the peculiar erosion of the walls into "chimneys," etc., and the enormous quantity of limonitic ochre which fills up the interstices of the breccia as a cement, seem to indicate the influence of stronger agents besides aerated and carbonated waters. The conversion of chalcopyrite into malachite, azurite, etc., of sphalerite into smithsonite, and of galenite into cerussite and anglesite, imply strong chemical action; and it has been suggested that "smithsonite may even now be forming in the ground to quite a large extent."[201] The known solubility of the lead sulphate and carbonate in solutions of citric and other organic acids adds to the probability of the natural agency of the latter in such veins. The concentration of certain ores, especially limonite, often auriferous, as a solid cap (eisenhut) to a vein just below the gossan, or as a cement to a breccia made up of fragments of the walls, is a further consequence of the superficial chemical changes which have been caused or assisted by organic acids. The contact-deposits, which in Europe are often of great economic importance, also represent such a concentration, *e. g.*, the iron-ores of the Northern Banat.[202] These consist of ferruginous

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[201] M. Strong, Geol. of Wis., 1877, II, 691.

[202] Von Cotta, *op. cit.*, 284.

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ammoniacal and alkaline salts, etc. These have effected extensive chemical and physical changes within the deposits, and often upon the material of the underlying stratum which constituted the island. The chief agency of the more complex organic acids, such as humic, crenic, etc., in these interesting changes, is shown by the following facts: that they only of the solvents present can dissolve some of the phosphates (*e. g.*, those of alumina and manganese), which enter largely into the composition of the guano: that the height of the mean annual temperature diminishes largely (by about a third) the content and solvent power of carbon dioxide in atmospheric waters usually obtaining in temperate climates: and that such acids as humic, crenic, etc., have been often distinguished in analyses of these guanos.

§ 52. *General results.*— The following are some of the principal effects which have been produced, mainly by the substances of acid nature dissolved in the meteoric waters: the concretionary aggregation of the amorphous materials, to which the deposits have owed their origin, both in the oolitic grains which constitute the superficial layers and pockets of the guano, and in the large and often huge concretions which are abundantly scattered throughout: the solution of phosphates of lime and their deposit in stalactitic forms in subterranean cavities: the solution and conveyance elsewhere of calcium-carbonate, commonly accompanied by a substitution of calcium-orthophosphate in its place, in fragments of corals, etc., enclosed in the deposit: and in the erosion of fissures in the underlying rock, especially when calcareous, and their contemporaneous occupation by phosphates, especially of calcium, carried down from above.

XVII. INFLUENCE UPON MINERALS.

§ 53. *Common alteration.*— All crystallized minerals in the superficial strata, both in the rock matrix, and lining geodes and veins, exhibit evidences that they have rarely escaped the influence in some degree of the action of organic acids. Often the loss of lustre on surfaces and cleavage planes, the stains and films of iron-ore and manganese-oxide, and even pitted surfaces and cellular material, decayed as by a kind of caries, reveal the action of such solvents. But even when the incipient alteration has not progressed so far, there may be chemical evidences, such as the gases clay, containing nodular masses of limonite and hematite, inserted between mica-schist and curiously eroded limestone, and in part of a limestone-breccia cemented by iron-ore and calcite.

In his discussion of the succession of minerals in lodes. founded on the simple action of carbon dioxide and water, Bischof[203] resorts to the influence of "organic matter" merely for the occasional *reduction* of ferric oxide, and yet confesses his perplexity in regard to the full explanation of the relationship of the modes of solution and transfer of silica and iron-oxide. But the consideration of the humic group of acids, as strong solvents of silica, appears to present the missing clew, both to the solution of silica *from quartz*, as well as from decomposed silicates in the rock, and to its frequent immediate deposition as the first layer of a lode; or, when air was present, to the oxidation of the ferrous oxide, which was after a time abundantly combined and conveyed in the same solvent, and the deposition of ferric oxide as the first layer, and the subsequent precipitation of silica as the second layer, on account of the further oxidation and dissociation of the constituents of the organic solvent.

XVI. ACTION ON GUANO DEPOSITS.

§ 51. *Presence of humus-acids.*—A conspicuous instance of chemical changes, due to the organic acids, is presented in the sub-aërial accumulations and vein-deposits of phosphatic guano, and in the underlying beds of coral-limestone, especially in regions with heavy rainfall. Baker's, Jarvis, Howland's, and other islands in the Pacific, St. Paul's and Ascension in the South Atlantic, and Monk's, Aves, Navassa, Swan, and Sombrero in the Caribbean Sea, have afforded interesting examples of these phenomena. My observations on the guano-deposit of the last-named island are yet to be published, but the following conclusions are pertinent here. A rich growth of vegetation, and sometimes even of forest, has generally clothed the surface of the loose arenaceous deposit; and even where this growth has since completely disappeared, the mass of the rock-guano is thoroughly permeated by innumerable minute tubular holes, produced by the decay of the rootlets. The decomposition of the abundant organic matter, both vegetable and animal, has yielded a continuous supply of organic acids, in addition to

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[203] *Op. cit.*, III, 543.

ammoniacal and alkaline salts, etc. These have effected extensive chemical and physical changes within the deposits, and often upon the material of the underlying stratum which constituted the island. The chief agency of the more complex organic acids, such as humic, crenic, etc., in these interesting changes, is shown by the following facts: that they only of the solvents present can dissolve some of the phosphates (*e. g.*, those of alumina and manganese), which enter largely into the composition of the guano: that the height of the mean annual temperature diminishes largely (by about a third) the content and solvent power of carbon dioxide in atmospheric waters usually obtaining in temperate climates: and that such acids as humic, crenic, etc., have been often distinguished in analyses of these guanos.

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§ 53. *Common alteration.*— All crystallized minerals in the superficial strata, both in the rock matrix, and lining geodes and veins, exhibit evidences that they have rarely escaped the influence in some degree of the action of organic acids. Often the loss of lustre on surfaces and cleavage planes, the stains and films of iron-ore and manganese-oxide, and even pitted surfaces and cellular material, decayed as by a kind of caries, reveal the action of such solvents. But even when the incipient alteration has not progressed so far, there may be chemical evidences, such as the gases of empyreumatic odor evolved and the darkening of color produced, on heating a fragment, *e. g.*, in hyalite and in many forms of hydrated ferric oxide. The fetid varieties of calcite, orthoclase, quartz, etc., always of superficial occurrence, seem to indicate the formation of a sulphide and impregnation with organic matter, both perhaps produced by acids derived from the overlying soil.

Several minerals appear to owe their very origin and existence, sometimes exclusively, to the action of the humus-acids. A few examples may be briefly considered.

§ 54. *Limonite.*—The economic importance of this product has caused the observation and record of an abundance of well-known facts. Its concentration in low grounds is commonly attributed to the leaching effect of organic acids upon ferruginous sands, etc., *e. g.*, among the dunes of Denmark,[204] near the rivers of Central Europe and in its northern lakes,[205] etc. The general phenomena have been carefully discussed by Hunt[206] and LeConte, and Dana has recognized the fact that the *main* solvents have been organic acids other than carbon dioxide.[207] Some particulars have been already given in regard to the class of limonite-deposits which have this organic origin, but the full discussion of my observations on this subject is for the present deferred. The large content of iron-ore deposits in organic matters has established this theory of their origin beyond question. The following are among the most significant examples: *humic acid*, in the limnite (bog ore) of Novgorod, Russia,[208] and of New York,[209] in the limonite of Westerwald,[210] and of Braunschweig[211] (12.5–14 per cent.): *apocrenic acid* (2.21 per cent.), *crenic*, and other acids (amounting in all to 15.01 per cent.) in an iron-ochre of St. Anne, Montmorenci, Canada:[212] *crenic acid* in a bog-ore of Smaland,[213] and *ammonium crenate* (4 per cent.), in an oolitic red iron-stone of Belgium:[214] *oxycrenic acid* (1–2.5 per cent.), in a limnite (bog-

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[204] Roth, *op. cit.*, I, 597.
[205] Bischof, *op. cit.*, I, 170.
[206] Essays, 13, 22, etc.: also Rep. Geol. Canada, 1863, 511.
[207] Man. of Geol., 1863, 361.
[208] R. Hermann, Erd. Jour. pr. Ch., 1842, XXVII, 53.
[209] Karsten, Karst. Arch., XV, 1.
[210] Ullmann, Ueb., 1814, 314.
[211] Wiegmann, Preischr. Torfes, 1837, 75, 76.
[212] T. S. Hunt, Rep. Geol. Can., 1863. 513.
[213] Gmelin, Handbook Chemistry, XVII, 466.
[214] T. L. Phipson, Compt. rend., 1861, LII, 975.

ore), of Novgorod, Russia,[215] etc. It is stated of the lake-ores of Sweden that they are "always deposited rather toward their banks than in the middle": indicating the almost immediate precipitation of the iron-oxide, on its introduction by drainage-waters from the neighboring hillsides, in the shallow and aerated waters, and in the black vegetable mud, along the shores.

The formation of limonite-ores is so strongly related to organic matters that it has long since been established by Logan, Hunt, etc., that the existence of deposits of iron-oxide of any kind may be taken as highly probable evidence of contemporaneous organic life. It has been further shown[216] that the amount of iron-oxide in recent sediments must be considerably decreased by that locked up in fossil deposits of ore: and, on the other hand, that the conditions for the accumulation of carbonaceous sediments are for the same reason more favorable in the more recent geological periods.

But another class of these ores of common occurrence has resulted from the re-working up and alteration of masses of the various other iron-ores back into their original form of limonite.

H. D. Rogers has made particular study[217] of interesting examples of this kind. A magnetitic slate of his Primal series was observed to be crossed by cleavage-fissures at right angles to the stratification, filled with limonite, which he says has been produced "by the copious admission of the surface waters and atmosphere into the body of the rock." In limonite-beds at various horizons, including the fossiliferous ore of the Surgent series, he attributes the origin of the hydrated ferric oxide to recent concentration in two ways: first, the decomposition of pyrite, the infiltration of waters impregnated with salts of iron, especially the sulphate, and final precipitation, as per-oxide, in contact with calcium-carbonate: secondly, and principally in the Surgent series, in beds of mingled ferruginous and calcareous materials, "the removal by infiltrating water of a part or all of the soluble portion of the ore, chiefly its carbonate of lime, both diffused and in the shape of innumerable organic remains." Many analogies render it probable, that, in both processes, the solvent action of organic acids has been largely concerned.

The conversion of siderite into limonite is a common mode of genesis, in this connection, and one in which the organic acids

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[215] Hermann, *idem*.

[216] Hunt, Essays, 229.

[217] Geol. of Pa., 1868, II, Part II, 718 to 733.

may be presumed to act as indispensable solvents, previous to the further oxidation of the ferrous carbonate. Many instances occur in this country in Massachusetts, Pennsylvania, etc., and abroad, in Bavaria, Transylvania, etc.

§ 55. *Pinite.*—There is a class of minerals of secondary and often pseudo-morphous character, *e. g.*, the pinites, which consist of insoluble aluminous residues, resulting from the removal of soluble bases, such as iron, lime, the alkalies, etc., from such minerals as the feldspars, hornblendes, etc. In at least one such case, the killinite of Chesterfield, Mass., as I have recently shown,[218] the solvent of the lithia from the parent spodumene has been an organic medium, probably a mixture of sodium and potassium azo-humates, which has penetrated into the granyte-veins of that region to the depth of at least fifteen or twenty feet, produced this interchange of soluble bases represented by the pinite, and left a notable content of nitrogenous matter in this and its associated minerals.

§ 56. *Sundry minerals.*—Attention has also been called by Dr. Bolton[219] to other minerals, whose incipient alteration or very formation may be referred to the acids of humus.

The green coloration of Amazon-stone from Pike's Peak, Colorado.[220]

The ferrous salt with organic acid diffused through cryptocallite (Dr. G. E. Moore).

The organic substance, containing nitrogen and carbon, which produces the color of smoky quartz.[221]

Whewellite, calcium oxalate ($2\ \mathrm{Ca\,O} + 2\ \mathrm{C^2\,O^3} + 2$ aq.), occurring in small crystals on calcite (Brooke).

Thierschite,[222] another calcium-oxalate, forming a "grayish warty, and somewhat opaline incrustation" on the columns of the Parthenon at Athens. Its origin is attributed to the action of lichens on the marble.

Humboldtine ($2\ \mathrm{Fe\,O} + 2\ \mathrm{C^2\,O^3} + 3$ aq.,) hydrous ferrous oxalate, forming an incrustation upon brown coal in Europe, and, in this country, upon bituminous pyritiferous schists, on Lake Huron. In the latter case, however, the oxalic acid may owe its origin to

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[218] Ann. N. Y. Acad. Sci., 1879, I, 340.

[219] Ann. N. Y. Acad. Sci., 1877, I, 34.

[220] G. A. Koenig, Proc. Acad. Nat. Sci., Phila., 1876, 155.

[221] A. Forster, Pogg. Ann., 1871, CXLIII, 173, 193.

[222] Liebig, Ann. Chem. Phar., 1853, LXXXVI, 113.

the action of sulphuric acid, derived from the pyrite, on carbonaceous material.

Mellite ($Al + C^{12} O^9 + 18$ aq.), or hydrous aluminum mellitate, containing over 40 per cent. of the organic acid, may share the same origin. It occurs in Europe on brown and stone-coals.

Pigotite ($4\ Al^2 + C^6 H^{10} O^4 + 27$ aq.),[223] a salt of alumina and mudesous acid, occurs as a brown incrustation upon the roof and sides of caverns, in the granitic cliffs on the east and west coasts of Cornwall, England. The organic acid is derived from the decay of various plants growing on the moist moorlands above, is carried down by the waters into the fissures of the granyte, and there combines with the alumina of the decomposed feldspar, and is deposited. It has also been found at Wicklow, Ireland.[224]

With these belong also the peculiar minerals grouped by Dana[225] under the names *oxygenated and acid hydrocarbons*, found in peat-bogs and in brown coal. They consist of the ill-defined bodies, Geocerite ($C^{28} H^{56} O^2$), Geocerellite ($C^{28} H^{56} O^4$), Brucknerellite ($C^{24} H^{44} O^8$), and Mellanellite ($C^{48} H^{40} O^{15}$ (?), supposed to contain ulmic acid), found in brown coal: and Butyrellite ($C^{32} H^{64} O^4$), and Dopplerite ($C^8 H^{10} O^5$? containing acids related to humic acid), found in peat-bogs.

In addition to these we may add that the carbonates (*e. g.*, Teschemacherite, $Am^2 O^5 + 2CO^2 +$ aq.), phosphates (Stercorite, Struvite, Brushite, Metabrushite, Ornithite, Zeugite, Kollophane, Vivianite), and nitrates (Nitre, Nitrocalcite, etc.), which occur in masses of organic matter, chiefly of animal origin, such as guano, the deposits in bat-caves, etc., here take their place.

Gibbsite, the aluminum hydrate, is occasionally associated, as attached crusts, with limonite, and must in those cases have shared in the peculiar mode of origin of the latter mineral.

The stalactitic deposits of hydrous aluminum-silicate, found in the caverns of Upolu in the Samoan islands, which "have resulted from the decomposition of lavas that overlie the caverns by percolating waters,"[226] have probably found their solvents in the rich soil which covers the surface.

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[223] J. F. W. Johnston, L. D. and E. Philos. Mag., 1840, (3), XVII, 382.

[224] Apjohn, Ch. Gaz., 1852, 378.

[225] *Op. cit.*, 738, 747.

[226] J. D. Dana, U. S. Expl. Exp., Geol., 1846, 323.

XVIII. RELATIONSHIP TO AMORPHOUS SILICA.

§ 57. *Modes of formation.*—The genesis of amorphous or hyaline silica in nature has been hitherto attributed to four agencies:

1. *Separation by the life-force* out of solution in both fresh and marine waters, resulting in the growth of organic deposits, chiefly the diatomaceæ, radiolariæ and polycystineæ. Interesting relationships prevail between the growth of these organisms and that of the bog-ores.

2. *Deposit from solution in thermal waters.* This mode of genesis has been carefully studied by many observers, and is illustrated by the geyserite and siliceous tufas of hot springs in Iceland, France, Colorado, etc., and by the veins of true opal produced by subterranean solutions.

3. *Precipitation by acids of solutions of the silicates.* This is a probable source of two forms of soluble silica. The first is developed in soils and loose deposits, probably in the form of zeolithic silicates, hydrated or otherwise, and easily decomposable (S. W. Johnson, How Crops Feed, 349 to 354: analyses of Heiden, Rautenberg, and Way). Bolton finds, by direct experiment, that the zeolites, prochlorite, etc.—about twenty common minerals—are decomposed by citric acid in the cold, *with separation of silica* (see table already quoted). The second consists of the amorphous silica, often in part still soluble, which serves as the cement of many sandstones, etc.

An investigation recently published[227] throws light on the bearing of organic acids in this direction. When a weak solution of oxalic acid is gently superposed upon a solution of sodium-silicate, there is formed, at the plane of contact, a siliceous layer possessing all the common physical properties of hyalite. Hardness, greater than that of glass. Sp. gr., 1.97: after heating at 30°–35°, with loss of hygroscopic water, 2.03–2.07. Transparent; after gentle heating, milky in color. Chemical composition: silica 87.9, combined water 9.9, soda and alumina 2.2 = 100.0. The author states, "by means of the superposition of liquids of different densities I believe certain mineral species can be reproduced; reactions can be thus imitated which are probably in progress at a slight depth below the surface of the soil and at a low temperature."

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[227] E. Monier, Compt. rend., 1877, lxxxv, 1053, and 1878, lxxxvi, 1318.

In addition to the three foregoing modes of genesis, hitherto accepted, I have now to suggest:

4. *Deposit from solution in organic acids*, especially the silico-azo-humic, derived from overlying humus and infiltrating through subterranean fissures. The hyaline silica, due to this source, has assumed two forms: the one, *hydrated*, hyalite, as a kind of vein-deposit, in crusts upon the walls of fissures: and the other, but in small part hydrated, as amorphous masses of flint, chert, etc.—within the body of limestone-strata.

§ 58. *Hyalite crusts.*—The prevailing opinion in regard to the distribution of a mineral in nature is apt to be influenced by the abundance of those of its varieties which are prized and searched after by miners, mineralogical collectors, etc. It is certain that hyalite, far from being rare, is a form of silica of exceedingly common occurrence, though almost always in small and inconspicuous quantity. A few instances of recent observation may be mentioned. From beneath the great overflow of diabasyte along the Hudson river, called the "Palisades," the underlying Triassic beds project at many points, in an altered condition, and have been styled "trappean schists." At Weehawken, N. J., I found the surface of the joints in this rock to be covered with hyalite in considerable abundance, in the form of thin crusts and rosettes. Color, shades of brownish-white to colorless. Sp. gr., 2.041, in coarse powder and distilled water at 67.5° F. Like hydrophane, it evolved minute bubbles of air in large numbers, on immersion in warm distilled water, and it required a continued immersion of 48 hours to expel them completely. On ignition, it lost 9.37 per cent. of water and organic matter, evolving empyreumatic and ammoniacal odors.

The conditions of its origin are simple. The surface of the talus of fallen fragments, at the base of the dyke, is overspread, sometimes quite thickly, with a layer of rich black humus, which is kept moist by streams trickling down from and through the vertical face of columnar trap. It is covered by a dense forest with thick shrubbery, and in many places supports a luxuriant growth of ferns, mosses, etc. The organic acids, developed in this rich forest-soil, are carried down among the fallen fragments of trap; and, partly by the decomposition of that rock, especially of its viridite and of the films of chlorite which coat the fissures, and, it may be, partly by that of the schists — in which analyses have shown a cement of opal-silica — the solution becomes saturated with silica, and redeposits it, by evaporation, as hyaline crusts upon the walls of the joints below. The trace of organic matter, which imparts the color of the mineral and its odor on ignition, evidently represents a portion of the organic solvent matter included in the gelatinous deposit during its desiccation. Similar thin crusts upon the surface of the trap, possessing a snow-white color and beautiful pearly lustre, have been obtained in the vicinity by Prof. D. S. Martin of New York, and it is probable that the mineral abounds along the whole dyke.

Again in many of the mica-mines of North Carolina, similar occurrences of hyalite have been observed by Dr. H. C. Bolton and myself. At Juggenheim's mine, on the North Toe river, in Yancey county, the walls of the joints of the granyte-veins were often covered with hyalite, in thin crusts of delicate yellowish-green color (caused by a small proportion of ferrous silicate), sometimes associated with and even overlying films of uranochre. A spectroscopic examination disproved the supposition that the green tinge was produced by uranium-oxide. Sp. gr., 2.00. Minute bubbles of air were expelled in great numbers on immersion in water, with increase of transparency. Loss by ignition, 8.35 per cent. It decrepitated slightly in a matrass, and yielded an empyreumatic odor and vapors that turn red litmus paper blue, *i. e.*, are ammoniacal. At the Puzzle mine, in Mitchell county, a hyalite of greenish-blue color occurred in similar crusts. At both localities, the surface of the ground, above the quarry, was clothed with an almost virgin forest and heavy undergrowth of rhododendrons, springing from a thick layer of rich black humus.

The analyses of opal and hyalite from various foreign localities frequently indicate the presence of nitrogenous organic matter and of ammonia.[228] Even the true opal of Mexico and Hungary evolves such decided empÿreumatic and ammoniacal odors, on ignition, that Damour[229] ventured to ascribe the peculiar reflections of the gem to the presence of carbonaceous matters.

§ 59. *Formation of chert, flint, etc.*—We have next to consider the influence of organic acids in the concentration of hyaline or amorphous silica within the mass of strata. Bischof,[230] Hunt,[231]

[228] Rammelsberg. Min. Chem., 1875, II, 164. See also Fournet, on "Organico-mineral colouring principles," Compt. rend., 1860, l, 1175: 1860, li, 39, 140.

[229] Ann. Min., 1840, (3), XVII, 207. [230] *Op. cit.*, II, 465, etc. [231] Essays, 89.

and others have treated of the separation of this substance from its solution in sedimentary deposits, as crystallized or chalcedonic sands, in the silicification of fossils, in beds of flint, etc. LeConte has recently suggested[232] that the silicification of wood, and perhaps the cementation of gravel, have been effected in California and elsewhere by the precipitation of silica in an insoluble form, through the neutralization of percolating alkaline solutions, charged with silica, by the humic, ulmic, and other acids of organic decomposition; the same process may very probably account for the siliceous cement in the interstices of many ancient sandstones, etc., especially if formerly rich in organic remains. The frequent and extensive silicification of wood in Tertiary deposits may have been, in many cases, therefore, connected with solutions of humus-acids during its decay, as well as with its recognized subsequent solution and re-deposition by thermal waters. Silicified trunks have been often observed in Colorado,[233] in which the material is found to be carbonaceous internally and at the heart passes into charcoal.

Many cherty layers probably owe their origin to the metamorphism of ancient infusorial deposits, and even their partial transport, by organic solvents, with an alteration often so complete as to nearly or completely obliterate the minute organic forms. Ehrenberg thus found[234] that the infusorial beds, near Kolt and Geistingen, do not contain any empty shells, but are all filled with siliceous substance; the tripoli and rottenstone, largely used in the arts, consist in great part of the frustules of Naviculæ and Pinnulariæ; and the polishing-slate of Bilin in Bohemia, and especially the well-known Turkey-stone, "seem to be essentially composed of a similar aggregation of frustules of Naviculæ, etc., which has been consolidated by heat."[235]

However, the origin of the chert and flint-layers which so strongly characterize the Carboniferous and Cretaceous strata, as well as many of Palæozoic age,[236] seems now to be better explained in the light of the revelations from the deep-sea ooze, already discussed, and of the approximate identification of the long-sought-for solvents of silica. The almost identical conditions

[232] Am. J. Sci., 1880, (3), XIX, 181, footnote; El. of Geol., 193.

[233] Letter from Capt. E. H. Ruffner, Fort Leavenworth, Kansas.

[234] Sitz. d. Berl. Ak. d. Wiss., 1846, May.

[235] Carpenter, The Microscope, 1875, 336.

[236] Dana, *op. cit.*, 377.

and materials which have been proved to exist, in the present as in the ancient Cretaceous seas, have acquainted us with all the steps in the process, depending upon time: from the recent mixed sediments, which contain up to 54.9 per cent. of silica, to its isolation in the flint-layers, out of a rock, the Chalk, the mass of whose material still retains very rarely as much as 3 or 4 per cent.[237] of silica, usually about half of one per cent.,[238] and this, apparently, no longer remaining in organized form.[239] The process has been well described in the following passage:

"In the chalk, which contains not a trace of silica, we often find the moulds and outlines of organisms which we know to have been siliceous, from which the whole of the silica has been removed; and I have more than once seen cases in which a portion of the delicate tracery of a siliceous sponge has been preserved entire in a flint, while the remainder of the vase which projected beyond the outline of the flint appeared in the chalk as a trellis-work of spaces, vacant, or loosely filled with peroxide or carbonate of iron. It therefore seems certain that *by some means or other* the organic silica, distributed in the shape of sponge-spicules and other siliceous organisms in the chalk, has been dissolved or reduced to a colloid state, and accumulated in moulds formed by the shells or outer walls of embedded animals of various classes. *How the solution of the silica is effected we do not know precisely.* Once reduced to a colloid condition, it is easy enough to imagine that it may be sifted from the water by a process of endosmose, the chalk-matrix acting as a porous medium, and accumulated in any convenient cavities."[240]

The means and mode of solution of silica, concerning which this author expresses doubt, in the passages I have italicized, can be now with some probability referred to albuminoid or glairy matters, and acids akin to the azo-humic of Thenard, produced during submarine decomposition of the organic matter infiltrating into and disseminated through the sediments. To this solvent agency may be also attributed the concentration of perhaps nearly all deposits of amorphous silica as chert, hornstone, etc., in other calcareous beds. It may also be suspected that the same organic

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[237] By analyses of D. Forbes, 1.10 per cent. in white chalk of Shoreham, and 3.61 per cent. in the grey chalk of Folkestone, Eng. (Depths of the sea, 514).

[238] E. T. Hardmann, Geol. Mag., 1873, X, 434.

[239] F. Kitton, Hardw. Sci. Goss., 1878, XIV, 277.

[240] Thomson, Depths of the Sea, 481.

agency may have been concerned in the formation of the Gaize of the Ardennes, a siliceous layer underlying the Cretaceous strata and sometimes 100 meters in thickness, containing from 29 to 47 per cent. of soluble silica.[241] If its origin, like that of the flint, has been submarine and contemporaneous with the deposition of the overlying sediments, we may conjecture the possible existence of a similar layer at a certain depth below the ooze of the present deep-sea deposits.

§ 60. *Other theories.*—Renard, however, in his recent excellent paper[242] on the *pthanites* (schistose chert-layers), in the Carboniferous limestone of Belgium, though he recognizes the important fact that "the silicification has taken place before the formation of the joints and fissures," offers the provisional theory that when "at certain intervals the waters of the Carboniferous sea holding in solution a solvent of the limestone, carbonic acid for example, attacked the calcareous matters, silicic acid was infiltrated into the calcareous sediments and impregnated them in proportion as they were decomposed." He further holds that the details of the micro-structure of the chert "prove also that it is impossible to admit, in order to explain the formation of the pthanites, as has been so often repeated in regard to flint, that these rocks are derived from the accumulation of organisms with siliceous envelopes." This he considers proved, both by the very exceptional enclosure of such organisms, for example in flint,[243] and by the difficulty of accounting, by that theory, for the perfection of their preservation. He therefore concludes: "finally we add that our pthanites present no analogy with the deposits of microscopic siliceous organisms pointed out by Ehrenberg, especially in Bohemia and in Sicily, nor with the siliceous sediments which the exploration of the deep seas has shown in progress of formation upon the bed of the ocean."

A somewhat analogous view has been also advanced in regard to the chert-beds in the Upper Carboniferous limestones of Ireland:[244] that at the close of the period of the latter, "the sea-bed was elevated, so as to be covered by the waters of a shallow sea, exposed to the sun's rays, and of a warmer temperature than

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[241] Compt. rend., 1870, LXX, 581, and 1871, LXXII, 767.

[242] Bull. de l'Ac. roy. de Belg., 1878, (2), XLVI, Nos. 9 and 10.

[243] J. Wright, Rep. Brit. Assoc., 1874, 95.

[244] E. Hull and E. T. Hardmann, Proc. Roy. Soc., 1878, XXVI, 163.

when at a greater depth:" that the waters became charged with an unusual supply of silica, derived from the siliceous rocks of the surrounding lands: and that a chemical replacement of silica for calcium-carbonate took place, the access of the sea-waters being facilitated by their warmth, by the porous character of the limestone, the softness of the ooze, etc.

But the conditions required by the latter theory must then have been very common, attending the formation of chert-beds of all ages; and yet no such saturation of sea-waters by silica is now known to occur. Such a deposit of silica would have developed transverse veins or aggregations of a crystalline material; and it could hardly have produced the isolated nodules and layers, amorphous material, and concretionary structure, presented in chert and flint.

In reply to Renard's argument, it may be remarked that purely calcareous beds, undoubtedly made up entirely of organic material, often present similar modes, both of obliteration and of the occasional protection and perfect preservation of certain individual organisms; and I have found, after the microscopical examination of very many thin sections of flint from France and England, that specimens are exceedingly rare in which no traces of organic forms may be detected, while those are very common in which the material is thronged by such forms, in various degrees of perfection. We may also expect in time to determine the conditions which have differentiated the deposition of colloid silica in the Cretaceous beds as flint, and in other limestones as hornstone, chert, chalcedony, jasper, agate, etc. Numerous examinations of these last amorphous or crypto-crystalline forms of silica, in thin sections, by polarized light, show a more distinct granulation than that of flint, often fibro-radial, and with much stronger refractive energy. This indicates, in the condition of genesis — or at least of the last metamorphism, a solvent and crystalline exertion which must naturally have accomplished the general obliteration of most of the more minute organic forms. Flint, hornstone, and amorphous chert, therefore seem to me to present *the colloid form of silica necessarily deposited from a solvent of a colloid nature*, such as humic[245] and probably the azo-humic acids have been found to possess. Granular chert, jasper, etc., on the other hand, appear to be the crystalline forms of silica,

[245] Detmer, *vide ante*.

probably in part deposited from solution in thermal waters, in the course of the metamorphism which has generally affected the pre-Cretaceous sediments in which they occur.

The universal presence of siliceous particles, in all the calcareous sediments now being deposited, seems fairly to justify the presumption of their presence in the ancient sediments. The conditions of decomposition within the sediments naturally differing in various parts, according to the character of the material, entrance of aerated waters, temperature, etc., the results of decomposition have also varied. In certain parts, the organic acids were probably largely developed for the solution of all adjacent silica, while elsewhere the organic matter was perhaps mainly destroyed and its place subsequently occupied in part by infiltration from the silica-solution.

Petzholdt has found[246] in the Silurian dolomitic beds of Lievland, that, where the average content of silica in the rock was 4.7 per cent., this content decreased to 2.3 per cent. in the close vicinity of the hornstone nodules. Bischof reasonably concludes from this[247] that the silica of the nodules has been derived simply from concentration of that in the surrounding rock; and his only question, which he does not attempt to answer, relates to the nature of the solvent,—in these beds as in chalk, the action of carbon dioxide being evidently not pertinent, nor the intervention, suggested by Dana, of the alkaline waters of the ocean.[248]

There seems no need to go outside of such sediments for the source of silica: all analogy renders it probable that its indigenous amount was sufficient. Ehrenberg and Murray, it is true, have recorded the silicification of foraminifera in the deep-sea ooze, the thin layer in direct contact with the sea-water; but the abundant supply both of silica and of decomposed organic matter, as its solvent, throughout the enveloping ooze, affords a satisfactory explanation of this phase of the process. Indeed, it is difficult to see how there could have been — as the theories of both Renard and Hardmann, above-quoted, require — especially before the formation of fissures and joints, the passage and diffusion of so great a volume of the sea-water, containing only 0.002 per cent. of silica,[249] through vast masses of the finest sediments, mostly consolidated and under enormous pressure, to furnish the enormous

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[246] Silicification organischer Körper, 1853, 20.
[247] *Op. cit.*, II, 490.
[248] Man. of Geol., 488.
[249] Roth, *op. cit.*, I, 505.

quantity of silica concentrated in the nodules of chert or flint. The negative considerations of Renard do not therefore seem to me to bear much weight against the overwhelming analogies which have been noted in the ancient and recent examples of the submarine aggregation of amorphous silica.

XIX. Periods of Special Activity.

Certain periods in geological time seem to have been especially characterized by the activity of the chemical reactions under discussion, as recently presented in some detail by Le Conte.[250]

§ 61. *Archæan.*— Hunt attributes the alternation of white feldspathic beds, poor in iron, with beds of iron-ore, to the intervention of organic matters, *e. g.*, in the Green Mountain rocks of Canada, and particularly in those of the Laurentian series, with their additional association of graphite. The exhaustion of iron-oxide from the Laurentian rocks, also pointed out, is indicated by their remarkable poverty in the oxide in a diffused form, which appears to have been concentrated in the heavy and numerous beds of ore. On these grounds, it has been claimed that "we may probably look upon the formation of beds of iron-ore as in all cases due to the intervention of organic matters; so that its presence, not less than that of graphite, affords evidence of the existence of organic life at the time of the deposition of these old crystalline rocks."[251]

The abundance of iron-oxide deposited in the Huronian sediments is illustrated by the fact, that, notwithstanding its common concentration in vast ore-deposits, the interbedded rocks remain highly basic and ferruginous.

There are indications in the Cambrian beds, which have induced the palæontologist to believe that "the earliest life of the globe must have been vegetable,"[252] and I think that the chemical results further prove the existence at that time of abundant land-vegetation. This may possibly have been cryptogamic, when we consider the established existence of algæ in the ocean-waters of that age, the ready transport of their spores, and their susceptibility to modification. The facts certainly indicate an amount of chemical action, revealed in the solution, transport, and deposit of iron-oxide, which was enormous, if not in intensity, at least in its accumulation by

[250] El. of Geol., 374. [251] Hunt, *op. cit.*, 13, 30. [252] Jukes, Man. of Geol., 439, 445.

time, and probably unequalled by the entire amount of similar action through all subsequent ages. And, although the conditions were not such as to render it the greatest of the Carboniferous ages, by the storing up of the element indicated by that name, the fact that the Archæan was of all others the Ferriferous age points as definitely to the vast antiquity of vegetable life, in the form of land-vegetation, and to the solvent action of the results of its decay — the humus-acids. The products of this action appear to have been three in number, — the iron-ores (chiefly magnetites), the aluminous strata, and a vast mass of siliceous sands — which afforded the materials worked over and over again,[253] by all agencies, throughout at least all Cambrian and Silurian time, to provide the hematites and limonites, the aluminous schists, and the siliceous quartzytes and sandstones of the earlier Palæozoic epochs.

§ 62. *Palæozoic.*—Throughout Palæozoic time the abundant occurrence of beds of iron-ore, in numerous localities, indicates the presence and chemical influence of the same organic agencies. Such ores, for instance, abound particularly, according to H. D. Rogers, in Pennsylvania, in the Primal, Auroral and Matinal, and Surgent series: and in Virginia, according to T. Egleston, in the Potsdam, Trenton, Clinton, Oriskany, and Hamilton shales. Rogers attributes these ores to the oxide derived from upraised Primal, or later sediments, washed down into the ocean along with calcium-carbonate.

The abundant deposits of limonite of the Great or Cumberland Valley, belonging to the Calciferous epoch, have attracted much investigation, resulting in diverse views concerning their origin. It has been explained[254] that they always rest upon impervious damourite-slates, which stopped the flow of ferruginous waters and occasioned the accumulation of these deposits. Whatever the source of the iron-oxide may have been, whether pyrite or other ferruginous minerals in the limestones, dolomytes, or other associated rocks, the action of humus-acids may be suspected in connection with this ore, *limonite*, their ordinary product. They have probably served for its transport, and as the erosive agents in the excavation of the numerous limestone-caverns (instead of that which has been suggested, the dissolving action of water containing ferrous sulphate). If it shall be possibly established that

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[253] Dana, *op. cit.*, 200.

[254] F. Prime, Jr., Am. J. Sci., 1875, (3), IX, 433.

the iron was first deposited as carbonate, its solution and decomposition were probably accomplished by these acids, previous to its oxidation and hydration.

In the Medina period of the American continent the coast region consisted of "low sandy seashores, flats, and marshes;" and in the Clinton period the widely spread beds of argillaceous iron-ore are proof, both of extensive marshes, and, although no plant-remains are known, of a land-vegetation and its decay, by which only the concentration of iron-oxide could have been effected.

During the Devonian, the beds of the Oriskany period in Nova Scotia also contain argillaceous iron-ores, now sometimes magnetic, which testify to a land-vegetation and humus-layer, notwithstanding the present absence of the remains of land-plants.

§ 63. *Carboniferous cherts and iron-stones.*— The decomposition of enormous quantities of vegetable matter, during the Carboniferous age, was accompanied by a vast development of the humus-acids, by a corresponding amount of chemical sub-aërial erosion in the superficial strata above the water-level, and by the deposit of large quantities both of ferric oxide *and of colloid silica.* It is a significant fact that the iron-ores of the coal-measures are *intimately associated with a chert or buhrstone*, and the ores of ferrous carbonate themselves contain, as collated from over fifty analyses given by Rogers, from about 6 to 60 per cent. of silica,[255] the more siliceous being termed "buhrstone-ore." The transport both of the iron-oxide and of this large quantity of colloid silica, represented by the chert, necessarily involves the agency of silico-azo-humic acids, in addition to the carbon dioxide considered by Rogers.

In the Carboniferous measures of England, the "seat-stone" of the coal-beds sometimes consists of a "very hard flinty rock," known as *ganister* in Yorkshire. In Upper Silesia and Poland "beds of clay iron-stone (spherosiderite) are tolerably common. They occur principally in those localities where numerous and thin coal-seams alternate with argillaceous shales. This clay iron-stone appears to be confined to the upper strata of the Carboniferous and near thin coal-seams. It is entirely wanting where thick coal-beds occur. It is to be accepted as a practical rule, that these iron-stones generally occur in the foot-wall of thin seams, and in

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[255] Geol. of Pa., 1868, II, Pt. II, 739.

the hanging wall of broad coal-beds. Still this rule has many exceptions."[256] The ores consist partly of argillaceous spherosiderite and partly of argillaceous limonite — the latter possibly formed by alteration of the former.

In considering the origin of the associated deposits of clay iron-stone, Bischof has pointed out[257] that "the formation of coal, proto-carbonate of iron, and other carbonates, may have gone on simultaneously" in argillaceous strata associated with the coal, on account of the excess of organic matter present: "but at the same time it must be understood that such a formation of carbonates could also have taken place after the coal formation was raised above the sea" by the reducing influence of the gases, gradually evolved during the subterranean decomposition and transformation of vegetable deposits into coal, penetrating original deposits of ferric oxide in clay-beds overhead.[258] Rogers accepts the latter theory for the formation of the iron-stone deposits in the coal-measures of Pennsylvania.[259] Recently, however, in his general and excellent discussion of the work of the humus-acids in the transport and concentration of iron-oxides, LeConte[260] rather dwells upon the initial deposit of ferrous carbonate as probable, merely under the condition of "the presence of excess of organic matter," both in recent peat-bogs and in those of the Carboniferous period. But it is an important fact, that, so greedy are solutions of ferrous salts for oxygen,[261] that recent instances of the permanent deposit of ferrous carbonate are *extremely rare*,[262] occurring only at chalybeate springs, never in bogs, and are always accompanied by conditions of perfect protection from the air, *e. g.*, by thick layers of clay or of ferric oxide derived from the oxidation of the carbonate itself. Again the known deposits of any form of iron-ores by bog-waters, now in progress, rarely occur in immediate contact with the beds of organic matter, but in separate basins, as in the Swedish lakes, or near the *outlets* of swamps and peat-bogs, where the aeration of the slowly flowing and highly dilute solutions causes the precipitation. The view

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[256] Von Cotta, Treatise on Ore Deposits, 244.

[257] *Op. cit.*, I, 315.

[258] *Idem*, 170–1; also German Suppl., 1871, 64–70.

[259] Geol. of Pa., 1868, II, Pt. II, 736–739. See also Von Cotta on a similar reaction in ores of the lower Cretaceous, Ore Deposits, 257.

[260] El. of Geol., 1879, 136–7, 374–5.

[261] Bischof, *op. cit.*, I, 155. Fresenius, J. pr. Chem., 1855, 64, 368.

[262] Bischof, *op. cit.*, I, 156–7.

adopted by Rogers seems to me therefore at present the more probable, since iron-stone deposits are never found in direct contact with coal.

In explanation of the general association of the iron-ore with thin layers of coal, it need only be stated, that the heaviest beds of coal imply the longer subsidence, deeper waters, enormous excess of organic acids, and absence of basins, comparatively free from the reducing and therefore solvent action of humus, for the reception of the precipitate of ferric oxide. On the other hand, numerous alternations of shale with thin layers of coal indicate also occasional shallow basins of more thoroughly aerated water, in which the iron-deposit could be thrown down: and that too in abundance, in the absence of thick beds of coal, as in the Upper Carboniferous measures of Silesia and Poland. Again the re-conversion of carbonate into hydrated ferric oxide reveals that the iron, which owed its first removal, transport, and concentration, to the solvent action of the humus-acids, was at a later period, after its transformation into ferrous carbonate, again subjected to their action in intermittent solution and oxidation.

§ 64. *Coloring material of sandstones.*—In England, the prevailing colors of the Upper Coal-measures are red, purple, and mottled red and green. "The rocks of which the group is made up are mainly shales and sandstones; it contains seams of coal, but they are neither so numerous nor so thick as those of the Middle Coal-measures."[263] In these red rocks each grain is enveloped by a thin skin of ferric oxide, implying its concentration in the waters in which these sands were deposited. Prof. Green hence concludes that the water was itself red as blood, on account of the suspended iron-oxide: that its retention was due to the closing up of the outlets of the lakes in which the sandstones and shales were formed: that the associated limestones, sometimes thinly laminated and occasionally possessing a porous spongy texture, were produced by precipitation of calcium-carbonate from solution in closed bodies of water: and that the source of the ferric oxide was volcanic, produced by the decomposition of iron-chloride, rising as a sublimate in the neighboring volcanic districts of the British Isles. The true explanation of the facts, however, seems to have been already suggested; and especially is there no need of ascribing to a volcanic sublimate the source of

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[263] Prof's Green, Miall, etc., "Coal, its History and Uses," 1878, 62–64.

the ferric oxide. The westward prolongation of the Archæan rocks of the Scandinavian peninsula, referred to by this author, probably covered by heavy vegetation and swamps, must have afforded an ample area and volume of ferruginous materials for the solvent action of humus-acids on a vast scale and through a long period, sufficient to have supplied the ochreous cement of the sandstones in the Carboniferous seas.

The principal investigation, of which I am aware, on the subject of the coloring material of such ferruginous sandstones, one so important in its relations to the modern accumulations of bog iron-ores, was made thirty years ago by Dawson, in reference to the red sandstones, and associated greyish and white beds, of the Lower Carboniferous formation in Nova Scotia, in which he comes to the following conclusions.[264] He recognizes that "the red coloring matter, which is the peroxide of iron, is in a very fine state of division, having indeed rather the aspect of a chemical precipitate than of a substance triturated mechanically." The source of the detrital matter of the sandstones, he finds in the Silurian, metamorphic and hypogene rocks, which have formed the ridges between the basins of deposit during the Carboniferous period: and that of the ferric oxide, in the pyrite disseminated through the immense masses of these older formations. During the alteration of the latter by igneous agents, he suggests that the pyrite in the superficial deposits has been converted into peroxide of iron and sulphuric acid, or sulphuretted hydrogen subsequently oxidized to sulphuric acid; and while the detritus was mainly colored through this agency by the iron-oxide, the acid was carried into the sea and combined with calcareous matter in the form of the present beds of gypsum. The decoloration, shown in the grey, dark, and white beds, he attributes to two possible causes, both acting contemporaneously with the process of deposition. First, in marine deposits, to the deoxidizing influence of decaying vegetable matter and the conversion of oxide of iron into sulphide, in the presence of the sulphates of sea-water. Of this he gives an interesting illustration from the decoloration of the reddish mud deposited by the streams upon the mud-flats, covered by eel-grass, in the harbor of Pictou, N. S. Secondly, in fresh water deposits, to "the action of acids produced in the

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[264] Quart. Journal of Geol. Soc., 1849, V, 25.

putrefaction and decay of moist vegetable matter," making reference to the phenomena presented in peat-bogs and swamps.

To the main theory I think it may be fairly objected that the concentration, especially to such a degree, of an unstable mineral like pyrite, among superficial detrital deposits, as well as its distillation in the manner suggested, is unprecedented and improbable. Again, the amount of pyrite disseminated through the ancient formations (if we take, like Dawson, the standard of its proportion in present unaltered remnants) is *by no means* sufficient to have supplied the immense quantity of ferric oxide in the later sediments. The same objection may be made to *magnetite*—to which Dana attributes the derivation of the iron-oxide in the Triassic sediments, apparently from the agencies attending the eruption of the trap-dykes (Manual of Geology, 1863, 432)—on the ground both of the insufficient amount of that mineral, and its refractory nature toward any agencies likely to have attacked it during the short duration of submarine volcanic eruptions. On the other hand, the ferruginous minerals, hornblende, chlorite, orthoclase, and the iron-garnets, not mentioned by Dawson, are characteristically prominent and abundant in the parent crystalline rocks of Archæan age, and even occur in the sediments, and are readily assailable by agents of decomposition. *Biotite* also abounds in Archæan rocks. Bischof calls attention[265] to its remarkable absence from most sandstones, notwithstanding their richness in muscovite, and attributes this to its more ready decomposition. J. W. Young detected the mineral only twice, in his examination of the Carboniferous sandstones of England,[266] but R. Lincke seems to have found it more commonly in the Triassic sandstones of the Thuringian basin.[267] The full explanation may be found in the observation of P. Schweitzer, in 1871, on the superficial decomposition of the gneiss of New York island, that "the black mica, after getting first coated with a brown film of oxide of iron, becomes rapidly disintegrated and disappears. The white mica possesses a much greater resistance, and abounds, therefore, in places from which feldspar and black mica have completely disappeared."[268] Little biotite has therefore passed into the sediments which compose sandstones, and even there has

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[265] Chem. and Phys. Geol., III, 113.

[266] Chem. News, 1868, III, 307.

[267] Jahresb. f. Min., 1871, I, 15.

[268] Am. Chem., 1874, IV, 444.

been often subjected, as the thin sections of the sandstones show, to the later attack of meteoric and organic agents of decomposition. In the alteration of this mineral we may therefore find an important source of the iron-oxide in the Carboniferous and most ferruginous sandstones.

§ 65. *Mesozoic.*—Throughout this age, especially during the Triassic and Cretaceous periods, the coal-measures and occasional beds of argillaceous iron-ore both testify to the same activity of the humus-acids.

In the Triassic beds an abundance of plant-remains occurs, and even beds of coal of considerable extent in India and New South Wales, and, associated with argillaceous iron-ore, in Virginia and North Carolina.[269] In the Jurassic, the numerous remains, not only of plants, but of insects, of insectivorous and herbivorous mammals, and of reptiles, "prove that the land was covered with foliage and swarming with life,"[270] and even beds of coal and iron-stone occur in the Oolite of England.[271] In the Cretaceous, beds of lignite abound, and even beds of good coal in the central part of British North America.[272]

It may be added that in the beds both of this and other ages, the evidences of numerous oscillations of level, shallow water, emerging flats, and dry land intervals — the abundant distribution of lignite-layers — and even the highly ferruginous sandstones and shales, testify sufficiently to the distribution of a sub-aërial humus-layer, and to the extensive erosion carried on by its organic acids.

§ 66. *Cenozoic.*—The increased extent of the dry land during the Tertiary period was attended, as is well known, by a mild and genial climate, and by a great development of terrestrial vegetation, both as to variety and luxuriance. This is now shown by the abundant leaf, lignite, and forest-beds, and even coal, iron stone, red-ochre, and the vast bodies of ferruginous sands and clays.

Again, after its interruption in the higher latitudes by the barren desolation of the Glacial epoch, perhaps with occasional return, during the warmer interglacial intervals so fully discussed by Croll and Geikie, there is every indication that the withdrawal of the ice-layer was ultimately followed by a heavy forest-growth, and, subsequently over certain areas, by the extension of bogs and marshes and the filling up of innumerable lake-basins by

[269] Dana, *op. cit.*, 418. [270] Dana, *idem*, 466.

[271] Jukes, *op. cit.*, 565, 576. [272] Dr. Hector, Quart. Jour. Geol. Soc., XVII.

peat.[273] The growth and decomposition of vegetable matter may have been further increased, as suggested by C. H. Hitchcock,[274] by the intercalation of warmer post-glacial periods. The accumulation and continuous decomposition of vegetable matters during this long period afforded the conditions for a remarkable amount of chemical alteration. This is represented by the deep disintegration of the rocks over all surfaces not swept by the ice-layer, as well as the wide distribution of bog-ores, infusorial earths, cherts, and other chemical deposits already sufficiently considered.

§ 67. *General review of the sandstones.*—In regard to the ferruginous material which occupies the interstices of the brown sandstones of America, it is important to notice, that, in the ochreous sands of Tertiary age and of the Drift, along the Appalachian border, this ferruginous cement appears to consist largely, perhaps chiefly, of *turgite:* that in the sandstones, both of the Triassic and of the Carboniferous, its chief component is *limonite:* but, in the Silurian beds, *e. g.*, the Shawangunk grits of Ulster Co., New York, the Potsdam sandstones on the shores of Lake Champlain, and the sandstones of the southern shore of Lake Superior, its bright, brick-red color and small loss of weight by ignition indicate its anhydrous condition and general identity with *hematite.* This last-mentioned state of the ferric oxide in the oldest of the Palæozoic sediments has been probably connected with their frequent deep subsidence and subjection to high thermal conditions. It is doubtless to derivation from the ground-up substance of these rocks that the red hard-pan of the drift of Minnesota and the surrounding region owes its iron-oxide, which, as N. H. Winchell points out,[275] exists in the anhydrous condition, while in the later clays the oxide is hydrated.

It therefore appears that the cementing iron-oxide in the ferruginous sandstones of each period exists *mainly* in the same state of hydration as the associated ores of *contemporaneous* origin. For the indigenous iron-ores of the Silurian, *e. g.*, in northern New York, Pennsylvania, Virginia, etc., and even yet a part of those of Archæan terranes, exist in the form of hematite; limonites afterwards predominate down to the Mesozoic; while in Tertiary and recent times, turgite is a characteristic accompaniment of other bog-ores.

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[273] N. H. Winchell, Proc. Am. Assoc. Adv. Sci., 1875, Pt. II, 43, and Geol. and Nat. Hist. Surv. Minn., 1875, 62.

[274] Geol. of N. H., III, Pt. I, 338.

[275] Geol. and Nat. Hist. Surv. Minn., 1876, 158, 172, and 1878, 85.

The differences in physical characteristics now obtaining in the sandstones of this class, under our observation, seem to be due but partially to those of the primitive mechanical sediments. They have probably had a twofold origin: first, in the most ancient sediments, by subjection to the extensive chemical action of the organic acids washed down from the swamps of the Archæan highlands: secondly, in the later sediments, by subjection to the same feeble but long-continued chemical action, since their elevation above the sea-level. Most of these rocks may be therefore considered as species illustrating one of the following stages in the process:

1. Green or gray detrital ("argillaceous") sandstones and flags, the original sediments derived from the degradation of crystalline rocks, passing into the "arkose" variety, where the latter are highly feldspathic and micaceous.

By the contraction of the uplifted Archæan area, in the Devonian and later ages, and consequently of the extent of humus-covered surface, the rate of chemical decomposition of detritus could not compete with that of the mechanical disintegration of fresh material: the resulting heavy accumulation of unaltered rock-detritus is well represented by the green flags and grits of the Devonian basins of central New York, etc.

2. Brown or red ("ferruginous" or "ochreous") sandstones. These comprise, almost exclusively, the vast accumulations of upper Devonian, Carboniferous, and later ages; and because still more rapidly and loosely aggregated and more porous than the preceding species, they are now found with their *silicated* mineral components in a partially altered condition. Thus they pass, by mottled or striped varieties, into

3. White ("siliceous") sandstones. These may thus find one source of derivation at the end of the process of exhaustion of originally argillaceous or ferruginous sandstones by percolating solutions of organic acids. But, on the other hand, the *most ancient* sandstones, those of Silurian and pre-Silurian age, as well as nearly all Silurian and Archæan quartzytes, whose strata mostly rest upon the flanks of broad terranes of Archæan rocks, appear to be made up of porous siliceous sediments which have been more or less thoroughly acid-washed during Archæan time. Familiar examples of these latter rocks are presented in most of the Potsdam sandstones, contiguous to extensive Archæan areas. It is stated in reference to the Potsdam that "the waters were shallow,

and that there were beyond doubt coasts and exposed sand and mud flats," with crustaceans crawling above the sea-level, indications of dunes, etc. Nevertheless it has been considered "an age without land vegetation to bind the soil," and that "there was no green herbage over the exposed hills."[276] However, the ferruginous and the purely siliceous sands, both indicate, in my opinion, the work of organic acids in the transport and exhaustion of iron-oxide; and it may be that the foraminiferal life, suggested by the glauconite of the period, also implies, for its nutrition, that trace of organic matter dissolved in the ocean, which must then as now have been largely derived from vegetation upon the land and along the shores. The coast at that period, like the margin of the North American continent at present, seems therefore to have been marked by a continuous fringe of land and tidal marshes for the partial purification of the loose detritus and the concentration of the pure siliceous sands in the outer beach, thence to be strewn over the bottom of the ancient sea.

XX. Conclusion.

The consideration of this subject at so great a length has seemed desirable on account of the prevailing disregard of the doubtless feeble and slowly working organic solvents, to which, in large part, such results may now be attributed. Yet the exclusive presentation, in this paper, of this single group of agents, may lead to the equally unfounded conclusion that the present writer, in his turn, has disregarded the efficiency, in many of the geological phenomena discussed, of the other well-known chemical agents of inorganic origin and nature. For the present, perhaps, no certain conclusions can be reached, in such cases, till more numerous and careful experimental researches shall have acquainted us with the precise genesis, character, and transformations of these substances. My present purpose has been chiefly to modify the views of those, who, like Bischof, look upon the main work of organic matter in nature as one of mere reduction, and who assign to carbon dioxide an exaggerated importance in that of solution.

My grateful acknowledgments are due to Mr. W. G. Baker, the librarian of the School of Mines, Columbia College, New York, and to Mr. R. Little, the Superintendent of the Astor Library, for special privileges and kind assistance.

[276] Dana, *op. cit.*, 196, 200, 203.