

*Citation:*

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which is in accordance with the formerly described localisation of the indigo-enzymes and of indican.

If woad is extracted without acid, so that the isatase can act, or with dilute alkalies, e.g.  $\frac{1}{2}$  pCt. solution of dinatrium phosphate, indoxyl is produced.

The necrobiotic stripe in partly killed woad-leaves results from the action of isatase on isatan.

**Geology.** — "*The Amount of the Circulation of the Carbonate of Lime and the Age of the Earth*". II. By Prof. EUG. DUBOIS.  
(Communicated by Prof. J. M. VAN BEMMELEN.)

In my first communication on this subject I have quoted a number of reliable data from which it follows that the waters of those rivers in whose drainage areas much limestone occurs, as is mostly the case with the larger rivers, are more than saturated with carbonate of lime, when reaching the ocean.

In consequence of their being polluted, to an extraordinary high degree, with organic matter, the quantity of carbonate of lime in the waters of many rivers of that kind, whose drainage areas are very thickly populated, in Europe and partly too in other parts of the world, is larger than in the primitive condition, before man existed in large number, thus during almost the whole past of the earth. In this respect I draw attention to the relatively higher quantity of carbonate of lime in such rivers as the Thames and the Seine, and also of the difference in that quantity between small and large rivers and lakes, as well as of some other facts showing the influence of the pollution of the water by organic matter on the relative quantity of dissolved carbonate of lime. The drainage water of soils, rich in humus, holds, for instance, considerably more carbonate of lime in solution than would correspond with saturation under the only influence of the atmospheric carbonic acid. But down the course of the rivers the last influence becomes by far the more preponderant.

Taking into consideration that in general the quantity of carbonic acid, produced by the decomposition of organic matter, increases somewhat at the mouths of the rivers, where much of that matter settles, and starting from the existing analyses, it seems to me that an average quantity of 95 mgrms. carbonate of lime per litre of water would represent, on the whole, with approximative accuracy, the primitive condition at the mouths of those rivers which have been so largely in contact with limestone that their waters could be saturated with carbonate of lime.

This ample contact of flowing waters with limestone seems to exist in almost every case, where true sedimentary formations predominate in their drainage area. Where, on the contrary, crystalline silicate rocks prevail in the drainage area, the quantity of carbonate of lime in solution decreases in the river-waters to a more or less lower amount.

According to the analyses by Kyle, quoted in my first paper, the Rio de la Plata keeps, 8 KM. above Buenos-Aires, per litre of water only 23 mgrms. carbonate of lime in solution. The drainage area of this large river consists for the larger part, by the side of Pampas-formation, of sandstones, Archean crystalline rocks and only little Palaeozoic rocks. The Amazonas, which, between the narrows and Santarem, keeps, according to the quoted analysis by Frankland, 27.5 and at Obidos, somewhat up the river, according to two other analyses, by Katzer, 11.4 to 14.6 mgrms. carbonate of lime in solution per litre of water <sup>1)</sup>, drains principally regions of gneiss, sandstones and clays. The same is the case with the Rio Pará (Tocantins), which, according to the analysis of a sample of the water from the harbour of Pará, taken during very low tide, keeps in solution 12.4 mgrms. carbonate of lime per litre of water <sup>1)</sup>.

The waters of most of the rivers and river-lakes mentioned in this and in my first communication, as examples of the kind keeping fewer dissolved carbonate of lime in solution than the quantity corresponding to saturation, have, however, not been exclusively in contact with silicate rocks, but also with some limestone.

The waters of some other, mostly small, river-lakes on the contrary, have not been in contact with limestone and derive the calcium carbonate they keep in solution entirely from the decomposition of silicate rocks or the desintegration products of silicate rocks. Such are those from the Lake of Starnberg, with 4.8 mgrms., Loch Katrine, with even much less than 4.8 mgrms., Reindeer Lake, with only a slight trace, and the Rachel-See, with 2.22 mgrms. calcium carbonate per litre of water; further the five named small French lakes with outlet, surrounded by granite and basalt, having a mean quantity of 8.9 mgrms. calcium carbonate in solution per litre of water.

For a comparison of the relative quantity of calcium carbonate in the five latter small river-lakes, draining regions of silicate rocks, with that of five equally small French river-lakes, in whose drainage

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<sup>1)</sup> F. KATZER, Das Wasser des unteren Amazonas. Sitzungsberichte der Kon. Bohmischen Gesellsch. d. Wissensch. Math. naturw. Classe. Jahrg. 1897. Prag 1898, N<sup>o</sup> XVII, p. 3—6 and 8.

areas limestone abounds, and which are likewise situated on a high level, I have dressed the subjoined table <sup>1)</sup>).

Lakes of	Height above sea-level, in M.	Volume, in millions of M <sup>3</sup> .	CaCO <sub>3</sub> , in mgrms. per litre.
Issarlès	997	60.0	10.0
Pavin	1197	23 0	15.7
Gérandmer <sup>2)</sup>	660	19 5	7 5
Chauvet	1166	17.3	6.5
Govivelle-d'en-Haut	1225	2.7	5 0
			Mean 8 9
Paladiu	501	97.2	150.9
Chalain	500	46.6	136 4
Nantua	475	40.1	155.5
Remotay	851	12.1	182 0
Sylans	584	4.8	152.6
			Mean 155.5

The mean relative quantity of CaCO<sub>3</sub> in solution in the latter group is 17.5 times as high as that of the first group of river-lakes.

Concerning the waters of the rivers and river-lakes, which have a higher relative quantity of calcium carbonate than those of the just mentioned lakes in granite and basalt, we can trace in most cases that, although they flow over crystalline rocks, they also have had an opportunity to dissolve some calcite.

So in the cases of the Rio de la Plata, which contains 23 and the Amazonas, which contains 11.4 to 27.5, of the Rio Pará, which keeps 12 4 mgrms. CaCO<sub>3</sub> in solution per litre of water, of the Dwina with 20.2, the Delaware with 25, the Croton River with 28.5, the Ottawa with 24.8, the Moldau with 19.4, the Uruguay with 16.2, Lake Superior with 30.8, Lake Tahoe with 23.2, Lake Baikal with 40.1 mgrms. CaCO<sub>3</sub> in solution per litre of water. The Hudson River, with 42 mgrms., is moreover connected through

<sup>1)</sup> The figures here quoted are also taken or calculated from the statements in DELEBEQUE's *Lacs français*. The reader will have noticed, that in the small table on p. 8 (51) of my first communication the volumes should be in *millions* of M<sup>3</sup>.

<sup>2)</sup> The quantity of CaCO<sub>3</sub> given here, which is also taken from DELEBEQUE's *Lacs français*, concerns the water of the surface, the formerly given the bottom water.

a channel with Lake Ontario, which is rich in dissolved carbonate of lime. For Lake Tschaldyr there is not sufficient information available to judge whether we have to think of the same mixture with dissolved  $\text{CaCO}_3$  or that the relatively high quantity of this matter is indeed to be interpreted by a particularly quick decomposition of silicates, as supposed in my first paper.

From all the available data it is evident that the quantity of calcium carbonate in solution in river waters is determined by the nature of the rocks with which they have been in contact. Indeed a great contrast is to be observed between the waters containing only the lixiviation products of crystalline silicate rocks and those flowing to some extent over true sedimentary formations. In the latter case the contact of the waters with limestone proves almost always sufficient to bring about a saturated solution of calcium carbonates.

If we estimate that in regions consisting entirely of crystalline silicate rocks — all other circumstances being equal — on an average *a tenth part* carbonate of lime is annually carried in solution by the flowing waters as in regions where limestone abounds, this estimate certainly remains rather below the real proportion.

Assuming moreover that the regions of the earth consisting of crystalline silicate rocks are on the whole in contact with as much flowing water as those where only true sedimentary formations are found — an assumption we may make with safety, as appears from the comparison of pluvial with geological maps — and taking, further, according to the figures given by Tillo, that the crystalline silicate rocks cover the fourth part of the land area of the globe, we find that the latter produce 9.5 parts carbonate of lime in solution at the same time as the remaining area of the land  $3 \times 95$  or 285 parts. According to this calculation the river-waters which are discharged into the ocean contain on an average 74 mgrms. carbonate of lime per litre and carry every year 2 billions (or  $2 \times 10^{12}$ ) K.G. carbonate of lime into the ocean, a value already mentioned in my first paper, though not yet explained.

According to this estimate the quantity of the calcium carbonate newly formed every year amounts only to a thirtieth (more exactly  $\frac{1}{31}$ ) part of the total quantity which the ocean receives every year. Annually there are thus formed from silicates 64.5 milliards (or  $64.5 \times 10^9$ ) K.G. of calcium carbonate, containing 28.4 milliards (or  $28.4 \times 10^9$ ) K.G. of  $\text{CO}_2$  in stable combination.

The earth having been evolved from a white hot liquid state, by cooling, and consequent envelopment with a solid crust, to its present state, we must assume that all the carbonate of lime arose

from the silicates of that crust. Silicic acid, being present in very great surplus in the crust of the earth, would, as is well known, already at boiling temperature of water have decomposed eventually extant carbonates. The formation of the crust, however, must have begun about 1000° C., for the melting-points of most silicates are between 900° and 1500° C.<sup>1)</sup> The carbonates, therefore, can only have come into existence after the formation of a solid crust of already considerable thickness. As shewn by Lord KELVIN, rather soon after beginning solidification the temperature at the surface of the earth must have been almost exclusively under the influence of the radiation of the sun. At the end of 100 years this temperature may have been about 8° C. higher, and at the end of 100 centuries 0.8° C. higher than without underground heat <sup>2)</sup>. We therefore may take it for granted that, considered from a geological point of view, the formation of the carbonates from silicates was initiated at the same time with the beginning of the condition of temperature, which made the earth an abode fitted for life.

If, therefore, we did know the average progress of this formation process as well as the total quantity of carbonates now extant, we should also know the time which has elapsed since the earth became fitted as an abode for life. As concerns the quantity of carbonates, besides the calcium carbonate, only the magnesium carbonate has to be taken into consideration; the other carbonates exist in relatively so small quantities, that in the very approximative calculations, concerned here, they may be neglected.

The proportion of the quantities of CO<sub>2</sub> in combination, as Ca CO<sub>3</sub> and as MgCO<sub>3</sub>, is for the water of the Rhine at Mayence <sup>3)</sup> probably about 3.3, for that of the Meuse at Liege 5.08, of the Danube at Vienna 2.36, of Thames <sup>4)</sup> at Kingston 8.33, of the Seine <sup>5)</sup> at Paris 5.17, of the Loire <sup>6)</sup> at Orleans 6.62, of the Spree <sup>7)</sup> above Berlin

1) J. Joly, The Melting Points of Minerals. Proceedings R. Irish Academy 1891, II., p. 44.

2) On the Secular cooling of the Earth. Transactions of the Royal Society of Edinburgh, Vol. 23. Compare also Lord KELVIN's latest paper on the subject: On the Age of the Earth. Annual Address for 1897 of the Victoria Institute of London, p. 21.

3) According to the analyses during a year by E. EGGER (Chemisches Centralblatt 1888, p. 1131 and Ref. in Jahresber. über die Fortschritte der Chemie. 1888, p. 2762.)

4) WITT, l. c., p. 116.

5) POGGIALE, ref. in Jahresber. über die Fortschritte der Chemie für 1855, p. 333.

6) BISSCHOF, l. c., p. 273.

7) ROTH, l. c., p. 457.

7.09 of the Vistula <sup>1)</sup> at Culm 5.28 of the Nile at Caïro probably about 3.00, of the Blue Nile at Khartoum 1.97, of the Syr-Darja 0.96, of the Rio Negro <sup>2)</sup> at Mercedes in Uruguay 5.44, of Lake Peipus 3.68, of the Lake of Geneva 3.08, of the Lake of Zurich <sup>3)</sup> 3.92, of the Lake of Bourget 4.42, of the Lake of Annecy 5.69 of St. Lawrence River 2.66, of the Lake of Gmunden 2.97, of the Lake of Saint-Point <sup>4)</sup> 11.55. The mean proportion in these twenty waters, which flow over true sedimentary formations, and are saturated with calcium carbonate, is 4.63. If this proportion, in which both carbonates are redissolved from sedimentary strata, also indicates the proportion in which they formerly originated in silicates, about  $\frac{1}{6}$  of the CO<sub>2</sub> consumed in the evolution of the carbonates would have been taken by MgO.

It appears to me that the following considerations may lead to an approximative estimate of the quantity of the carbonic acid consumed and fastened in these carbonates.

It is most probable that all the oxygen, which now partakes of the composition of the atmosphere, and even more, has entirely originated in carbonic acid gas through the assimilation process of the plants. In the rocks composing the earth's crust there is a great deficiency of chemically fixed oxygen, which would not be the case if in the former, hot, state of the earth there had been a sufficient quantity of oxygen available. According to CLARKE's analyses <sup>5)</sup> the rocks which compose the earth's crust consist on an average of 3.44 pCt. of FeO, thus an incompletely oxydized combination of iron. From the analyses of 83 basalts and diabases, published by ZIRKEL <sup>6)</sup> and ROSENBUSCH <sup>7)</sup>, a mean percentage of 6 FeO is to be calculated, from the analyses of 29 granites a mean of 1.5 pCt., of 47 gneisses a mean of 3.8 pCt. Starting from the proportion given by CLARKE we may estimate, that all the O of the atmosphere would

<sup>1)</sup> BISSCHOF, l. c., p. 275.

<sup>2)</sup> SCHOELLER, l. c., p. 1787.

<sup>3)</sup> ROTH, l. c., p. 457.

<sup>4)</sup> The Lake of Saint-Point, through which the Doubs flows, and whose water, having a volume of 81,6 millions of M<sup>3</sup>., is renewed in 205 days, contains, according to DELEBECQUE (Les Lacs français, p. 202) 136.4 mgms. CaCO<sub>3</sub> per litre of water.

<sup>5)</sup> F. W. CLARKE, The relative Abundance of the Chemical Elements. Bulletin 78, United States Geol. Survey. Washington 1891, p. 37 and Ibid. No. 148. 1897, p. 12.

<sup>6)</sup> F. ZIRKEL, Lehrbuch der Petrographie. Zweite Auflage, Leipzig 1893. Band II, p. 29 and p. 901; Band III, p. 80 and 223.

<sup>7)</sup> H. ROSENBUSCH, Elemente der Gesteinslehre, Stuttgart 1898, p. 78, 308—309 and 468—471.

only be sufficient to oxydize the FeO that is contained in the earth's crust to a depth of less than  $\frac{1}{2}$  K.M. All the parts of the crust, which are no true sedimentary formations, up to the surface, are, however, rich in FeO.

In the reduction of carbonic acid through the plants there having been made free an equal volume of oxygen, and the oxygen in the atmosphere having a volume 700 times as large as that of the carbonic acid therein, there must have been in or passed through the atmosphere at least 700 times as much carbonic acid as it contains at present. Another quantity of the oxygen made free through the agency of the plants, which quantity it is impossible to estimate, was certainly consumed for the oxydation of FeO and other constituents of the crust which are poor in oxygen.

It appears, therefore, that when the earth was in the white hot fluid state there could not exist any free oxygen. That which was not combined with carbon or hydrogen would have been taken by FeO, and as there is still much FeO, certainly to a depth of many K.M., in the earth's crust, apparently at the beginning formation of that crust no free O can have been in the atmosphere. The quantity now in the atmosphere must be rather less than that formed from the consumption of free CO<sub>2</sub> reduced through the agency of the plants, for younger sediments are certainly poorer in FeO, and must therefore have consumed O. There has, however, at the same time with that oxydation, taken place reduction of combinations of iron by organic matter. The clay deposited by the Rhine in the Delta of the Lake of Constance contains, besides 1.66 pCt. organic matter, 3.23 pCt. FeO; slates from the carbonic formation, besides 0.7 pCt. organic matter, 4.73 pCt. FeO<sup>1)</sup>. In consequence of this reduction again CO<sub>2</sub> is coming into the atmosphere, from which again O is set free through the agency of the plants. So from 1 volume of CO<sub>2</sub>, which originally was in the atmosphere, there may be formed 2 or more volumes of O<sup>2)</sup>. That reduction of Fe<sub>2</sub>O<sub>3</sub> combinations takes place on a grand scale is proven by the existence of the blue mud, which covers an area 37.6 millions of K.M.<sup>2</sup> or more than  $\frac{1}{10}$  of the floor of the ocean, and which owes its colour to organic matter and FeS<sub>2</sub>. Also the slates contain much FeO; as the mean percentage of 16 slates, of which the analyses are given by CLARKE, 3.25 is to be computed. In the waters of the larger rivers and

1) ROSENBUSCH, l. c., p. 413.

2) Of course only a superior limit for the amount of coal and other carbonaceous remains of organic origin in the earth's crust may be deduced from the 700 a parts of CO<sub>2</sub>, which have passed through the atmosphere, as the C of these has, in such a manner, been made use of several times.



lakes, on the contrary, are to be found in solution combinations of  $\text{Fe}_2\text{O}_3$  only.

But whatever may be the source of the  $\text{CO}_2$ , from which the O of the atmosphere has been set free through the assimilation process of the plants — for another process, which can produce O on a large scale in nature we cannot imagine — we must take it for granted, that an equal volume, that is at least 700 times the quantity of free  $\text{CO}_2$  now extant in the atmosphere, has been in it, and most probably has gradually passed through it. Now too the supply of carbonic acid, through the volcanic activity of the earth (which certainly is the chief source) and the consumption, through the fossilisation of carbonaceous organic remains, and in still much higher degree that through the formation of carbonates, which according to the above made estimate now annually requires  $\frac{1}{75400}$  of the quantity of carbonic

acid in the atmosphere<sup>1)</sup>, take place gradually. In all past times that consumption, as is shewn by the immense carbonaceous formations of organic origin and mighty strata of carbonate rocks, has been so large that we hardly can imagine but that this consumption and the supply from the interior of the earth have been equipoising processes.

Now SCHLÆSING<sup>2)</sup> has shewn, that for water which keeps in solution other salts (of natrium, magnesium, calcium) the quantity of the bicarbonate formed may be different from that formed in pure water, but that nevertheless, as in the latter case, it increases with the tension of the carbonic acid gas, so that there arises again a state of equilibrium between it and the tension of the carbonic acid gas. SCHLÆSING, further, pointed out that in the water of the ocean, which since many thousands of centuries has been in contact with the atmosphere and with the calcium carbonate of its floor, its shore and the supply of the rivers, there is a continual tendency to acquire this equilibrium. Variations in the quantity of the carbonic acid of the atmosphere will cause emission of carbonic acid from the ocean-water and severing of solid carbonate, if the variation is a decrease, or absorption of carbonic acid and dissolving of carbonate, if the variation is an increase. SCHLÆSING then calculated the quantities of carbonic acid contained in free state in the atmosphere, and in

<sup>1)</sup> The amount of the carbonic acid in the atmosphere is taken in this calculation at 2140 billions KG. (which value is equal to  $75400 \times 28.4$  milliard) from the averages stated below for the percentage of carbonic acid and the atmospheric pressure.

<sup>2)</sup> TH. SCHLÆSING, Sur la constance de la proportion d'acide carbonique dans l'air. Comptes rendus des séances de l'Académie des Sciences. 1880. Tome 90, p. 1410—1413.

loose chemical combination in bicarbonate in the ocean. He found that the ocean keeps in reserve, and at disposal for exchange with the air, a quantity of carbonic acid ten times as large as the total quantity which the atmosphere contains, and concluded therefrom that the ocean exercises a regulating influence on the quantity of the carbonic acid of the air, acting as a reservoir which holds a quantity of carbonic acid at disposal very much larger than the quantity which constitutes the variation in the air.

The volume of the water of the ocean is, however, much larger than SCHLÖESING had assumed. Computed from the most recent and reliable data for the area and the mean depth of the ocean it comes to 1300 million K.M<sup>3</sup>. If we accept the mean quantity of loose carbonic acid of 43.6 mgrms. per litre of ocean-water, according to DITTMAR, the mean atmospheric pressure at the surface of the earth of 740 mM. and the mean percentage of carbonic acid in the air, in volume, for both hemispheres, according to MÜNTZ and AUBIN <sup>1</sup>), of 0.027385, we find that in the ocean there is, in combination as bicarbonate, 26,5 times as much loose carbonic acid and also 26.5 times as much carbonic acid in stable combination as in the air in free state. Starting from the whole quantity of 55 mgrms. carbonic acid in stable chemical combination per litre of ocean-water, stated by DITTMAR, or from that of 53 mgrms., according to other statements, we further find, that in the water of the ocean 33.4 or 32.2, say 33 times, as much carbonic acid is in solution, in stable combination in calcium carbonate and bicarbonate, as the quantity of the free carbonic acid contained in the atmosphere. The quantity of the bicarbonate, however, alone is dependent on the pressure of the carbonic acid.

There being in the ocean 26.5 times as much loose carbonic acid as contained in free state in the atmosphere, the ocean has of every variation in the total quantity of carbonic acid by far the largest share. Of 27.5 parts carbonic acid which are to be disposed of or which are consumed, it always takes or gives 26.5 parts, and it has done so as long as its volume, its composition and its mean temperature and the pressure of carbonic acid did not differ much from the present state. Slight modifications of the pressure of carbonic acid, such as most probably have only taken place, can neither have had any noticeable influence. If, in fact, the quantity of the free carbonic acid in the atmosphere even changed with 60 pCt., the quantity of the carbonic acid taken up by the ocean in loose combination, according to the

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<sup>1</sup> l. c., p. A 82.

law of SCHLÖESING, would only vary with 16 pCt. or about  $\frac{1}{6}$ . Calling the quantity of the loose  $\text{CO}_2$  in the ocean  $o$ , that of the free  $\text{CO}_2$  in the atmosphere  $a$ , we find that  $\frac{o}{a}$  would come to 19.23 instead of 26.5. To 1 part of free  $\text{CO}_2$  in the atmosphere, the ocean would then only contain 19.23 parts of loose  $\text{CO}_2$  in combination as bicarbonates, i. e. 0.725 of the actual proportion. In order, however, to cause this variation of 60 pCt. in the pressure of the carbonic acid in the atmosphere, the production or the consumption should undergo a variation of  $0.6 \times 19.23$  or more than 11.5 times the quantity of carbonic acid at present in the atmosphere. Variations of the quantity of carbonic acid in the atmosphere of so great an amount, that they might have considerable influence on the value  $\frac{o}{a}$  are therefore indeed highly improbable, as it appears that the consumption of carbonic acid regulates itself after the production.

As pointed out by HÖGBÖM <sup>1)</sup> production of carbonic acid chiefly takes place by volcanic exhalations and geological phenomena connected therewith, and consumption by the formation of carbonates from silicates on weathering. "As the enormous quantities of carbonic acid, representing a pressure of many atmospheres, that are now fixed in the limestone of the earth's crust cannot be conceived to have existed in the air but as an insignificant fraction of the whole at any time since organic life appeared on the globe" the consumption through formation of carbonates and the storing up in sedimentary formations of carbonaceous remains of organisms must have been compensated by means of continuous supply, that is to say the two processes must always have nearly counterbalanced each other. May it be that the mentioned source of carbonic acid has not flowed regularly, but, just as single volcanous, has had its periods of relative rest and intense activity, and has produced now less, then again more carbonic acid, on the other hand also an increase of the supply surely causes an increase of the consumption. But even the relatively slight alterations of the quantity of carbonic acid in the air, which according to HÖGBÖM may still be allowed, are entirely prevented by the vegetable world. The decomposition of  $\text{CO}_2$  through the green plants varies with the tension of that gas in so high a degree, and the absolute quantity of  $\text{CO}_2$  which annually is decomposed by the vegeta-

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<sup>1)</sup> Quoted by S. ARRHENIUS, On the Influence of Carbonic acid in the Air upon the Temperature of the Ground. Philosoph. Magazine. Vol. 41, (1896) 5th. Series, p. 272.

tion is so large (namely about  $\frac{1}{20}$  of the whole quantity in the atmosphere) that soon the former percentage of  $\text{CO}_2$  in the air, on which plant life is regulated, would be restored.

On account of the facts discussed in this and in my first paper we may assume, that certainly not more than one thirtieth part of the carbonate of lime, which the rivers now discharge into the ocean is newly formed from silicates. In the past, when still more silicate rocks lay uncovered at the surface of the earth, this quantity must have been larger. At the time the earth's crust consisted still entirely of them, the carrying of newly formed carbonate of lime would, under otherwise similar circumstances, certainly not have been more than *one eighth part* of the quantity of the carbonate of lime now carried by the rivers to the ocean, and which is by far the greater part only circulating (redissolved) carbonate of lime. As the silicate rocks have gradually been covered with sedimentary strata that proportion must gradually have got smaller. If we take the most simple and most probable case, that this decrease took place proportionable to the time, then on an average 0.08 of the present annual carrying of calcium carbonate by the rivers would every year have been newly formed, thus 160 milliards (or  $160 \times 10^9$ ) K.G., containing 70.4 milliard (or  $70.4 \times 10^9$ ) K.G. of  $\text{CO}_2$  in stable combination.

In the long run the consumption of  $\text{CO}_2$  for the formation of carbonates from silicates and that for the formation of oxygen are to be considered as two processes, parallel in their magnitude, which, if other circumstances do not vary, are dependent on the pressure of the carbonic acid in the atmosphere. It is clear that the oxygen which only circulates through the plants is not concerned here, the circulating oxygen again serving for the oxydation of organic matter, just as the circulating calcium carbonate does not consume any carbonic acid, there being used for the formation of bicarbonate as much as is set free again when it returns into the solid state. However, to 700 *a* parts of free carbonic acid, consumed for the storing up of oxygen, in the atmosphere,  $26.5 \times 700$  or 18550 *a* parts must have been liberated from bicarbonates in the ocean, and thus at least 18550 *a* parts of carbonic acid in loose, and an equal quantity in stable chemical combination have been in bicarbonates redissolved from solid carbonates.

When thus at least 700 *a* parts of free carbonic acid in the atmosphere have been turned into oxygen, there must have been consumed in the waters of the rivers and the ocean at least  $26.5 \times 700 \times 0.08$  or 1484 *a* parts carbonic acid for the carbonates newly formed from silicates. Thus we find that, from the time the globe, by cooling, has been sur-

rounded by a solid crust, *at least* 7.22 trillion (or  $7.22 \times 10^{18}$ ) K.G. calcium carbonate have been formed which, equally spread over the whole area of the land of the globe, would be able to form a layer of limestone everywhere about 20 M. thick<sup>1)</sup>. Of course this is only a minimum, as the value 700 *a* also is a minimum. According to the estimates of MELLARD READE<sup>2)</sup> and DANA<sup>3)</sup> the mean thickness of the limestone under the land area of the globe would be 28 to 52 times as large. Assuming that the rivers carry to the sea on an average 450 mgrms. per litre or 6 times as much matter in suspension and in solution as they do carbonate of lime in solution, this proportion would lead us to impute to the sedimentary rocks under the continental areas an average thickness of about 3000 to 6000 M., certainly no too high estimates.

The time required for the evolution of that minimum amount of carbonate of lime from silicates it is, after these considerations, very easy to estimate.

In the same way as the quantity of the bicarbonates in the ocean, the average quantity of the bicarbonates in the river-waters is dependent on the pressure of the carbonic acid in the atmosphere. So the *ratio* between the average quantities of the bicarbonates, which the rivers have annually carried into the ocean, and the total of those which were in solution in the ocean is independent of the pressure of the carbonic acid in the atmosphere. Whatever variations the pressure of that gas in the atmosphere may have undergone, at any time in the past history of the earth the ratio between the quantities of those salts in solution in the ocean-water and the river-waters was not changed thereby. Further there must exist between the total quantities of the redissolved and the newly formed bicarbonates, which in the ocean have ever passed from the dissolved into the solid state, the same ratio as in the river-waters, for the ocean-water owes its provision of those salts to the rivers. As now the rivers carry annually two billion K.G. calcium carbonate in solution, containing  $\frac{1}{2432}$  *a* carbonic acid, a total amount of  $18550 \times 2432$  or 45 million times that quantity, in combination in calcium carbonate, has in the ocean passed from the dissolved into the solid state.

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<sup>1)</sup> Reckoned on a basis of 8 pCt. impurity.

<sup>2)</sup> Limestone as an index of Geological Time. Proc. Royal Soc. Vol. 28. London, 1879, p. 281.

<sup>3)</sup> L. c.

Therefore the formation of the whole estimated minimum amount of carbonate of lime on the earth would require about *forty-five millions of years*, that of the real amount, however, a very much larger lapse of time.

It appears, furthermore, that  $\frac{1}{2.770.000}$  of the total quantity of the carbonate of lime of the earth participates annually in the present circulation.

The amount of carbonic acid corresponding to the limestone rocks and carbonaceous formations in the earth's crust has been estimated very differently, namely between 12.000 and 15.0000 times the quantity of free carbonic acid contained in the atmosphere. The newest estimates differ somewhat less from one another. HÖGBOM <sup>1)</sup> considers it as probably underestimated, if we take that 25000 as much carbonic acid is fixed in the limestone of the sedimentary formations as exists in free state in the atmosphere. DANA <sup>2)</sup> calculates the quantity of carbonic acid, corresponding to the limestone and to the coal, mineral oils and gasses in the earth's crust on 45 atmospheres, that is 100.000 times the quantity of free carbonic acid in the atmosphere. CHAMBERLIN <sup>3)</sup> estimates, without indicating his method, that quantity on 20.000 to 30.000 *a*. At all events these geological estimates all differ too much from the minimum of 1484 *a*, calculated above by indirect way, that the presumption should not been raised — if indeed the bases of these estimates are in some degree reliable — that the value 700 *a*, from which the present calculation started, is only a minimum, and that indeed very much oxygen from the atmosphere has been taken away by oxydation of substances in the earth's crust which are poor in oxygen.

On the calculated number of 45 millions of years some corrections are to be made. Firstly this number should be diminished with at least a sixth part, because the carrying of carbonate of magnesia through the rivers has not been taken into account. Secondly the eroding agency of the ocean has not been considered; the ocean too assailing, at its border, silicate rocks and the forming of carbonates taking place there too. But thereby the number can decrease only little, as the eroding influence of the ocean is but slight compared to the agency of the waters on the land. DE LAPPARENT <sup>4)</sup> estimates

<sup>1)</sup> l. c. p. 271.

<sup>2)</sup> J. D. DANA, Manual of Geology. Fourth Edition. New-York 1896, p. 485.

<sup>3)</sup> T. J. CHAMBERLIN, Journal of Geology, Chicago 1897, p. 656.

<sup>4)</sup> A. DE LAPPARENT, Traité de Géologie. 4me Édition. Paris 1900, Tome I, p. 242.

the proportion on less than 1 : 10 and JULY <sup>1)</sup> even on 1 : 177. Thirdly the rivers may have discharged more water during the prevailing of warmer climates, thus during the longest time of the past of the earth. Neither can this influence, by which the stated number would get smaller, have been considerable, for, according to figures given by MURRAY <sup>2)</sup> the rivers under the present conditions discharge — at equal drainage area — in the area of the land between 30° North and 30° South of the equator on an average only 1.55 times as much water as outside of the 30° North and South. It therefore would certainly be too high an estimate assuming that, at the time when over the whole earth a tropical climate prevailed, the discharge of water, and therefore too the carrying of calcium carbonate (which at higher temperature of the water is even somewhat less soluble) had been one and a half time as high as at present. Fourthly the weathering of silicates and the formation of carbonates may have been more rapid on account of the temperature having been on the whole higher, of a more abundant supply of carbonic acid or of more rapid changes in orographic and hydrographic conditions. These factors too would diminish the stated number, but probably not considerably. Fifthly the ocean has originally been less salt; though already in such old formations as the cambrian mighty beds of rock-salt occur, a proof that in this factor is not to be sought the cause of important changes in the absorbing power of the ocean for carbonic acid, and therefore, by modifying the proportion  $o : a$ , of the time required for the formation of the limestone rocks, a modification that would also diminish the stated number. Sixthly a higher average temperature of the ocean-water would decrease the proportion  $o : a$ ; at a homogeneous tropical climate of the earth probably about 20 pCt., with which amount the estimated time also would have to be diminished. Seventhly the volume of the ocean-water could have decreased; but the analyses of the rocks show that in such a manner at most a decrease of a few hundredths parts could have taken place. On the contrary much water is produced in volcanic exhalations and connected geological phenomena.

All those influences, however, which would decrease the result of this time estimate, apparently do not counterbalance together the one influence of the loss of oxygen from the atmosphere by the oxydizing of Fe O and similar substances poor in oxygen, so that

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<sup>1)</sup> An Estimate of the Geological Age of the Earth. Scientific Transactions Roy. Dublin Society. Vol. VII (Series II). Dublin 1899, p. 63.

<sup>2)</sup> l. c., p. 70.

it appears, that we may assume, that the formation of the carbonates from silicate rocks has required *at least some decuples of millions of years*, and this the earth's crust also exists at least the same length of time. But this is a minimum; the real lapse of time since the formation of a solid crust and the appearance of life upon the globe may be *more than a thousand million of years*.

This final result of the investigation, however little claim it may make to exactness, might nevertheless interest geologists and biologists, who generally demand such a vast space of time. Moreover this result would be of some importance, if it should suggest nearer trial of the so called physical methods of estimating the age of the earth, by which Lord KELVIN has acquired unperishable merit for geology and biology, a trial which in many other respects too is desirable and promises important results. In his already quoted latest paper on this subject <sup>1)</sup> Lord KELVIN estimates the age of the earth's crust, on the basis of these methods, at about 24 millions of years, and the sun he estimates about as old. It seems possible to modify some factors in the calculations of Lord KELVIN in such a way that higher results are obtained. The here sketched geological method appears to confirm that opinion. May it therefore be further worked out and lead to a more exact estimate of the age of the earth as an abode fitted for living beings than the estimates hitherto obtained.

**Zoology.** — "*Further results of an investigation of the Monotreme-skull*". By J. F. VAN BEMMELLEN, The Hague (Communicated by Prof. C. K. HOFFMANN).

### I. *Palate.*

In a former note <sup>2)</sup> the curious fact was mentioned, that in the Echidna-skull the pterygoids form part of the floor of the cerebral cavity, filling up a gap between the body of the sphenoid bone and its posterior or temporal wings (alisphenoids), so as to be visible on the inner side of the skull-bottom. To this we may now add, that the same is the case with the palatine bones. In a skull, in which the majority of the sutures could still be distinctly traced, a slender posterior process of the palatine was seen running down on

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<sup>1)</sup> On the Age of the Earth, p. 11 and 25.

<sup>2)</sup> These Proceedings. October 25<sup>th</sup> 1899. p. 81.