SOME GEOCHEMICAL STATISTICS.¹

By FRANK WIGGLESWORTH CLARKE.

(Read April 20, 1912.)

More than twenty years ago, in a paper on the relative abun dance of the chemical elements,² the present writer compared a number of averages of analyses of igneous rocks, representing different regions, and showed that they were essentially identical. From these averages, combined into a general average, the mean composition of the igneous part of the lithosphere was computed, and the result obtained has since been confirmed by the study of much larger masses of data than were originally attainable.³ Other estimates, made by other computers upon similar lines, have since served to check my own, thereby giving to my conclusions a high degree of probability. The figures obtained have received a fairly general acceptance, and have served as a basis for other computations of a fundamental character.

This acceptance, however, has not been universal. The process of averaging analyses is criticized by several writers,⁴ who urge that it is unphilosophical. An analysis of a dike rock is given the same weight as that of a widespread and important formation, whereas each rock should be weighted in accordance with its volume. But we do not and probably cannot know these volumes, partly because detailed surveys are lacking, and partly because a surface outcrop fails to tell us what bulk of rock may lie below. If we try to estimate the volumes of the many rocks represented in the average, or

¹ Published by permission of the Director of the U. S. Geological Survey.

² Bull. Phil. Soc. Washington, 1889, Vol. 11, p. 131. Also in Bull. 78, U. S. Geological Survey, 1891, p. 34.

⁸ See Bull. 491, U. S. Geological Survey, "The Data of Geochemistry," pp. 22-27.

⁴See, for example, Daly, *Proc. Amer. Acad.*, 1910, Vol. 45, p. 211; Loewinson-Lessing, *Geol. Mag.*, 1911, p. 248; and Mennell, *Geol. Mag.*, 1904, p. 263, and 1909, p. 212.

even the areas exposed, we shall find ourselves relying in great part upon arbitrary assumptions, a procedure fully as unphilosophical as that which it would supplant. Estimates of that and similar kinds have been made, most recently by Loewinson-Lessing, whose figures give essentially the same result as that obtained by the method he has criticized. The method by volumes is doubtless ideal, but impracticable; and the true, philosophical procedure is to do the best we can with the available data. It is highly probable that the rocks of minor importance will balance one another, the persilicic and subsilicic varieties occurring in something like equal proportions. This supposition is sustained by the groups of average analyses which will presently be given. If we trust to individual judgments, different observers will reach widely different conclusions. Loewinson-Lessing supposes that the average rock may be about the mean of an average granite and an average basalt; Daly⁵ argues in favor of a fundamental basaltic magma; Mennell, whose experience has been gained in a granitic region, regards granite as the dominant rock with all else of minor importance. Mennell makes a strong argument in favor of his contention; but there is weighty evidence against it. If we study recent lavas, that is, the rocks which issue from unknown depths far below the surface, we shall see that rhyolite, the effusive equivalent of granite, is much rarer than andesite or basalt. The Deccan trap, the Columbia River basalt, the andesites of South America, the lavas of Iceland and the Hawaiian Islands are good illustrations of this statement. Moreover, the river waters which originate in areas of crystalline rocks contain almost invariably an excess of lime over soda, which would hardly be the case were granite predominant. Much socalled granite is really either quartz diorite or quartz monzonite, rocks which are probably far more abundant than has been commonly supposed.

In order to test the method of averaging analyses we may now compare the averages so far obtained by different computers, and then pass on to averages of rocks from distinct and widely separated areas. In these averages only the more important constitu-

⁵ Bull. U. S. Geol. Survey, No. 209, 1903, p. 110.

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ents of the rocks are considered, for the reason that the less conspicuous components have not been generally determined. They will be separately discussed later. All the means have been recalculated to 100 per cent., and water, for obvious reasons, is excluded. The methods for the determination of water are far from being uniform, and the variations are so great as to obscure the essential agreements between the other figures. The first table contains the following averages.

- (A) The average of 248 "superior" analyses of igneous rocks selected by Washington from Roth's tables. See U. S. Geol. Survey, Prof. Paper No. 28. Average computed by the present writer.
- (B) The average of 536 British rocks, computed by Harker."Tertiary Igneous Rocks of the Isle of Skye," Mem. Geol. Survey United Kingdom, 1904, p. 416.
- (C) Washington's average of 1,811 rocks from all parts of the world. U. S. Geol. Survey, Prof. Paper No. 14, p. 106.
- (D) Loewinson-Lessing's estimate of a mean between an average granite and an average basalt. Inserted here for comparison with the other columns.
- (E) The average of all the data relating to the composition of igneous rocks contained in the laboratory records of the U. S. Geological Survey. Computation by F. W. C.

. Alexing a	A	B	C	D	E
SiO ₂	61.13	60.49	58.83	60.17	61.68
Al ₂ O ₃	15.03	15.81	15.97	15.43	15.41
Fe ₂ O ₃	3.50	4.90	3.36	3.55	2.67
FeO	4.38	2.77	3.91	4.07	3.55
MgO	2.86	3.81	3.88	3.62	3.97
CaO	4.81	4.95	5.27	5.63	5.02
Na ₂ O	3.75	3.26	3.95	3.24	3.49
K ₂ O	3.32	2.84	3.19	2.82	3.07
TiO2	.78	.53	1.05	.89	.77
P2O5	.25	.22	.37	.35	.27
MnO	.19	.42	.22	.23	.10
	100.00	100.00	100.00	100.00	100.00

The general agreement is striking, and Loewinson-Lessing's estimate fits well in with the others. The next table is devoted to the

igneous rocks of North America, and the analyses are nearly all taken from the Survey records.

- (F) Average of 250 analyses of rocks from the Atlantic slope, Maine to Georgia. 78 of these are taken from Washington's tables, the others were made in the Geological Survey.
- (G) Average of 113 analyses of rocks from the Yellowstone Park.
- (H) Average of 137 analyses of rocks from Colorado.
- (1) Average of 195 analyses of rocks from California.
- (J) Average for all North America. The figures of column E combined with those of 398 analyses given in Washington's tables.

	F	G	H	I	J
SiO ₂	59.16	61.22	62.87	62.20	61.47
Al ₂ O ₃	15.17	16.35	16.66	15.87	15.63
Fe ₂ O ₃	2.16	3.30	2.67	2.12	2.67
FeO	5.36	2.58	2.40	3.46	3.22
MgO	4.92	3.47	2.06	3.93	4.02
CaO	5.69	4.95	4.01	6.06	5.12
Na ₂ O	3.46	3.83	4.11	3.49	3.62
K ₂ O	2.76	3.22	4.10	1.92	3.06
TiO ₂	.98	.69	.74	.58	.81
P ₂ O ₅	.23	.31	.27	.27	.27
MnO	· .II	.08	.II	.10	.11
	100.00	100.00	100.00	100.00	100.00

For Europe the following data are sufficient, all the figures, except Harker's, having been taken from Washington's tables.

- (K) Harker's average for British rocks, as previously cited.
- (L) Average of 231 analyses of rocks from Norway, Sweden and Finland.
- (M) Average of 420 analyses of rocks from the German and Austro-Hungarian Empires.
- (N) Average of 250 analyses of Italian rocks.
- (0) General mean of the foregoing 1,427 analyses, plus 122 of rocks from parts of Europe not otherwise covered.

Good analyses of rocks from Asia, Africa and Australia, at least as given by Washington, are too few for satisfactory combination. In the next table I give a general average for North

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	K	L	М	N	0
SiO ₂	60.49	60.84	58.83	60.18	59.89
Al ₂ O ₃	15.81	16.70	15.76	15.88	16.07
Fe ₂ O ₃	4.90	3.75	3.96	3.90	4.18
FeO	2.77	2.68	3.75	3.44	3.18
MgO	3.81	2.10	4.09	2.82	3.59
CaO	4.95	4.39	5.73	5.83	5.30
Na ₂ O	3.26	4.98	3.74	3.36	3.70
K_2O	2.84	3.68	3.18	4.17	3.25
TiO ₂	.53	.63	.67	.10	.51
$P_2O_5 \dots \dots$.22	.14	.22	.21	.20
MnO	.42	.11	.07	.11	.13
a landara	100.00	100.00	100.00	100.00	100.00

America, South America and Europe, South America being represented by the average of 82 analyses cited by Washington. The weights assigned are stated under each column.

	J, N. America.	P, S. America.	O, Europe.	Q, General Mean.
SiO ₂	61.47	61.13	59.89	60.76
Al ₂ O ₃	15.63	16.29	16.07	15.87
Fe ₂ O ₃	2.67	3.76	4.18	3.40
FeO	3.22	2.93	3.18	3.19
MgO	4.02	3.18	3.59	3.78
CaO	5.12	5.54	5.30	5.23
Na ₂ O	3.62	4.01	3.70	3.67
K ₂ O	3.06	2.16	3.25	3.08
TiO ₂	.81	.66	.51	.67
P ₂ O ₅	.27	.14	.20	.23
MnO	.11	.20	.13	.12
a man a there and see	100.00	100.00	100.00	100.00
Weight	8	I	7	

The last column may be taken as probably representing, with certain obvious limitations, the average igneous rock of the entire visible position of the lithosphere. The agreement between the preceding columns is so close as to suggest that similar averages from other parts of the world are likely to be of the same general order. It is hardly conceivable that analysts, dealing with rocks from such diverse regions as Colorado, South America, Germany, Great Britain, etc., should *select* subsilicic and persilicic rocks or salic and ferric rocks, in nearly identical proportions. The selection has been made by nature itself, and although there are differences indicating the existence of petrographic provinces, they are so slight as to leave

the essential identities unobscured. Some human selections are indicated in certain regions; for example, in Norway, the high soda is due to the disproportionate attention paid to the nepheline syenites; while in Italy the leucite rocks of Vesuvius lead to an apparent excess of potash. In the mean for all Europe these differences balance each other.

The general agreement between the several averages is well brought out by means of the method developed in the quantitative classification of igneous rocks. For this comparison, Professor Iddings has kindly made the necessary computations, with the subjoined results: Duplications of averages are of course avoided.

Average.	Column.	Magmatic Symbol.	Name.
Roth. Harker. Washington. Loewinson-Lessing. Survey. Atlantic Coast. Yellowstone Park. Colorado. California.	A B, K C D E F G H I I	II. 4. 2. 3. II. 4. 3. 3. II. 5. 2. 3. II. 4. 3. 3. II. 5. 3. 4. II. 4. 3. 4.	Adamellose. Harzose. Monzonose. Harzose. Tonalose. Andose. Tonalose. Adamellose. Tonalose.
North Europe. Central Europe. Italy. N. America. S. America. All Europe. General mean.	L M J P O Q	II. 5. 2. 4. II. 5. 3. 4. II. 5. 2. 3. II. 4. 3. 4. II. 5. 3. 4. II. 5. 3. 4. II. 4. 3. 4. II. 4. 3. 4. II. 4. 3. 4.	Akerose. Andose. Monzonose. Tonalose. Andose. Tonalose Tonalose.

In brief, all the averages fall in class II., dosalane, and in orders 4 and 5, but near the boundary between the two. The principal variations are in the rangs and sub-rangs, and are mainly due to the varying proportions of the alkalies. The average rock may be classed as tonalose, or, to use a more familiar term, as andesite. It is evident that in order to have any statistical validity, such averages as are given here must represent fairly large areas, and a considerable number of analyses. Small areas, especially those of volcanic islands, may vary widely from the mean; for example, analyses of 32 Hawaiian rocks gave in the average, only 48.55 per cent. of silica. Such local variations, however, could hardly exert any noteworthy influence upon the continental averages which represent

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more truly the general magma. They would be balanced, or more than balanced, by other areas of granitoid or dioritic character.

The tables so far given serve only to show the probable uniformity of the accessible magmas. In order to complete them, a number of minor constitutents of igneous rocks must be considered; which, however, have only been determined with adequate frequency in the laboratory of the United States Geological Survey. For example, in round numbers, 1,100 nominally complete analyses have here been made, and in 736 of them barium oxide was determined or proved to be absent. The mean of these determinations, counting absences as zero, is 0.100 per cent., which may be a maximum. If the remaining 364 rocks were all free from barium, and so regarded, the mean percentage of BaO would be 0.067, a minimum. Between these two figures the most probable value would lie, but nearer the maximum than the minimum, the mean being 0.084. Upon this basis of computation the following table of percentages has been constructed.

	No. of Determ.	Maximum.	Minimum.	Mean.
BaO	736	0.100	0.067	0.084
SrO	616	0.040	0.022	0.031
Li ₂ O	577	0.011	0.005	0.008
NiO	287	0.027	0.007	0.017
Cr_2O_3	270	0.050	0.012	0.031
$V_2O_3\ldots\ldots$. 87	0.024	0.002	0.013
S	748	0.112	0.076	0.094
F	98	0.100	0.010	0.055
C1	260	0.062	0.015	0.038
ZrO ₂	305	0.025	0.007	0.016
CO ₂	662	0.490	0.330	0.410

It is evident that these figures are not of equal significance. Some of them rest upon too few determinations, especially those for fluorine and vanadium. The experience of the Survey laboratory, however, leads me to believe that vanadium is very widely diffused in the igneous rocks, and that the mean assigned to it may possibly be exceeded. Chromium, nickel and zirconium are also more abundant than they were formerly thought to be. As for carbon dioxide, the figure given is probably much too high, for its presence in igneous rocks is mainly but not entirely ascribable to

alteration. The maximum for CO_2 , 0.49 per cent., may nevertheless be admitted in computing the composition of the entire lithosphere, as an allowance for carbonaceous matter which would otherwise escape attention. Copper does not appear in the table, but it is sometimes determined, and the order of its abundance is perhaps about the same as that of lithium, say 0.01 per cent. Boron, possibly, ought also to be taken into account, but it is seldom estimated, and no figure can be assigned to it. As for water, which up to this point has been neglected, the average shown by the Survey analyses is 1.95 per cent. This figure, which is excessive so far as the unaltered igneous rocks are concerned, may, however, be taken as including the water enclosed in the lithosphere and not otherwise estimated. The-allowance is ample.

Including the minor constitutents, the Survey analyses alone give the subjoined mean composition for that portion of the lithosphere which is represented by rocks of igneous origin. The total is recalculated to 100 per cent.

SiO ₂	. 59.85
Al ₂ O ₃	. 14.95
Fe ₂ O ₃	. 2.59
FeO	3.45
MgO	. 3.85
CaO	4.87
Na ₂ O	3.39
K ₂ O	2.99
H ₂ O	. I.92
TiO ₂	.75
CO ₂	48
P ₂ O ₅	
MnO	10
Minor constituents	.54
	100.00

This differs from the general mean already given under column Q in that it includes only the Survey data, and takes account also of water, carbon dioxide, and the minor constituents of igneous rocks. The important values, however, are all of the same order of magnitude in both estimates. The undetermined elements cannot aggregate over 0.5 per cent., and represent minor corrections which may

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be considered at some future time when suitable data are at hand. For present purposes they are negligible.

The mean composition of the sedimentary rocks has been determined in a different way. Composites of many samples were prepared and analyzed as if they were single samples, a method which saved much labor and was as satisfactory as if numerous individual analyses had been made. The data thus obtained have been repeatedly published, except in the case of the shales, for which a new estimate is here given. The analyses, recalculated to 100 per cent., are as follows:

 (A) Composite of 78 shales plus 45 individual analyses taken from the laboratory records of the U. S. Geological Survey.
123 shales in all.

- (B) Composite analysis of 253 sandstones.
- (C) Composite analysis of 345 limestones.

	А	B	C
SiO ₂	59.23	78.33	5.18
Al ₂ O ₃	15.68	4.76	.81
Fe ₂ O ₃	3.59	1.07	3 51
FeO	2.85	.30	5 .24
MgO	2.71	1.16	7.90
CaO	2.58	5.49	42.57
Na ₂ O	1.27	.45	.05
K ₂ O	3.14	1.31	.33
H ₂ O	4.97	1.66	.77
TiO ₂	.65	.25	.06
CO ₂	2.40	5.02	41.54
P ₂ O ₅	.15	.08	.04
MnO	.05		.05
Minor constituents	.73	.12	.16
	100.00	100.00	100.00

These three columns represent the three dominant types of sedimentary rocks, and differ from the figures given the igneous rocks in certain losses by leaching, mainly of lime, magnesia and alkalies, and in a gain of water and carbon dioxide received from percolating waters and the atmosphere. There is a small increase in volume consequent upon the gains; the materials lost are principally to be sought for in that universal reservoir, the ocean.

For the relative proportions of the sedimentary rocks several

estimates have been made, which, however, can only be regarded as rough approximations to the truth. By studying the way in which an average igneous rock can break down, I have computed that the shales form 80 per cent., the sandstones 15 per cent., and the limestones 5 per cent. of the total.⁶ Van Hise⁷ distributes them as 65, 30 and 5 per cent. respectively, and Mead,⁸ by a graphic process, has found 80, 11 and 9 per cent. Combining the composite analyses just given in accordance with these ratios the following mean values are obtained for the total composition of the sedimentaries. The fourth column contains the average of the three separate estimates.

Contract of the second	Clarke.	Van Hise.	Mead.	Average.
SiO ₂	59.39	62.29	56.47	59.38
Al ₂ O ₃	13.30	11.67	13.14	12.70
Fe ₂ O ₃	3.06	2.69	3.04	2.93
FeO	2.33	1.94	2.31	2.19
MgO	2.74	2.50	3.00	2.75
CaO	5.01	5.46	6.50	5.65
Na ₂ O	1.09	.96	1.07	1.04
K2O	2.73	2.45	2.69	2.63
H ₂ O	4.27 .	3.77	4.23	4.09
TiO ₂	.56	.42	.55	.51
CO2	4.75	5.15	6.21	5.37
P ₂ O ₅	.13	.12	.13	.13
MnO	.05	.05	.05	.05
Minor constituents	.59	.53	.61	.58
	100.00	100.00	100.00	100.00

The first of these averages is the most probable, since it harmonizes best with the mean composition of the igneous rocks. If we reduce it to the form adopted for the latter, by rejecting its accessions, carbon dioxide and water, and also neglecting the minor constituents, it may be compared with the average marked E as follows:

	gneous E.	Sedimentaries.
SiO ₂	. 61.68	65.70
Al ₂ O ₃	. 15.41	14.72
Fe ₂ O ₃	. 2.67	3.38
FeO	. 3.55	2.58
MgO	. 3.97	3.03
CaO	. 5.02	5.54

^eU. S. Geol. Surv., Bull. 491, p. 31.

¹ U. S. Geol. Surv., Monograph 47, p. 940.

⁸ Journ. Geol., 15, 238.

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	Igneous E.	Sedimentaries.
Na ₂ O	3.49	I.2I
K ₂ O	3.07	3.03
TiO ₂	77	.62
P_2O_5	27	.14
MnO	10	.05
	100.00	100.00

This comparison shows an increase in silica, due to concentration Alumina is lowered, iron is nearly constant although the proportions of the two oxides are reversed, and potassium is constant also. Soda and magnesia show losses due to leaching. Lime is increased, which suggests that the 5 per cent. of the sedimentaries assigned to limestone is probably too high. Mead's estimate of 9 per cent. is certainly excessive. The largest uncertainty is due to the facts that the composite shale used for analysis did not include certain magnesian rocks, and the limestones did not embrace the dolomites. The deficiency of magnesia, however, is mainly to be found, with the soda, in the ocean. On the whole the comparison is satisfactory, although the lowering of the alumina is unexplained. The least satisfactory feature of the combination is the average composition of the shales; but even here the percentage of soda is probably good. In the important igneous rocks the proportion of soda varies within narrow limits, and any combination of them would yield sedimentary residues in which that oxide should show much the same relative loss. The Survey average for soda (column E) gives 3.49 per cent. The mean of 100 rhyolites given in Washington's tables yields 3.48 per cent., while for 220 basalts the percentage is 3.24. From the preceding table the ratio between igneous and sedimentary soda is 1.21 to 3.49, an order of magnitude which is not likely to be very much changed. The influence of certain variations in it will be considered later.

From the quantity of sodium in the ocean the mass and volume of igneous rock needed to furnish it are easily computed, and also the similar data for the sedimentaries. The oceanographic data are fortunately quite good, even though they may not be rigorously exact. The mean density of sea water, according to Murray, is 1.026, and its average proportion of saline matter is 3.5 per cent. by

weight. For the volume of the ocean there are several estimates. In my former calculations it was taken as 302,000,000 of cubic miles, while Murray found a larger figure, 323,722,150 cubic miles. These values, however, are now supplanted by later and more definite estimates, as follows: According to Karstens,⁹ the volume of the ocean is 1,285,935,211 cubic kilometers, or 308,509,000 cubic miles. Krümmel,¹⁰ still later, estimates the volume as 1,329,945,870 cubic kilometers, or 319,087,500 cubic miles. From these figures, with density 1.026, the mass of the ocean is as follows:

Karstens, 1,319,369,526,436,000,000 metric tons.

Krümmel, 1,364,524,469,802,000,000 metric tons.

The saline matter, 3.5 per cent., is therefore:

Karstens, $46,178 \times 10^{12}$ metric tons.

Krümmel, 47,758 × 1012 metric tons.

Puting the specific gravity of the oceanic salts at 2.25, their volume is easily found by the subjoined equation:

$$\frac{3.5 V \times 1.026}{100 \times 2.25} = x,$$

in which V represents the volume of the ocean. The value of x then is,

With Karstens' volume 4,923,800 cubic miles.

With Krümmel's volume 5,092,600 cubic miles.

The second of these values, derived from Krümmel's estimate of the volume of the ocean, represents a quantity of saline matter which would cover the entire surface of the earth, 197,000,000 square miles, with a layer 136.5 feet deep, or 468 feet over the land area alone. Figures like these show that the salts enclosed in the rocky crust of the earth are, in amount, relatively insignificant.

From Dittmar's analyses of sea water, made for the reports of the Challenger Expedition, the mass of each radicle contained in the oceanic salts can be calculated. In the following table I give Dittmar's percentage composition of the salts, and in a second column the weights corresponding to the total mass of $47,758 \times 10^{12}$ metric tons as found from Krümmel's figure the volume of the ocean.

⁹ Inaugural Dissertation, Kiel, 1894.

¹⁰ Encyclopedia Britannica, 11th ed., Vol. 19, p. 974.

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	Per Cent.	Metric Tons ×10 ¹² .
Cl	55.292	26,406
Br	188	89.8
SO4	7.692	3,673.5
СО3	207	98.8
Na	30.593	14,611
К	1.106	528.2
Ca	1.197	571.7
Mg	3.725	1,779
	100.00	47,758

The average specific gravity of 958 igneous rocks, collected in Washington's Tables, is 2.737; and one cubic kilometer of rock should therefore weigh 2,737,000,000 metric tons. From the average of the Survey analyses given on p. 221 ante, the mean percentage of sodium in igneous rocks is 2.51, and from Washington's average 2.90. Hence the sodium contained in the ocean, $14,611 \times 10^{12}$ metric tons, would be furnished by the complete decomposition of the following volumes of igneous rock:

From the Survey average, 212,680,000 cubic kilometers.

From Washington's average, 184,080,000 cubic kilometers.

Some sodium, however, remains in the sedimentary rocks, namely, 0.90 per cent. as computed from the *reduced* average analysis. On comparing this figure with those for the total sodium of the igneous rocks, the volumes of the latter actually decomposed become, approximately,

Survey, 318,950,000 cubic kilometers.

Washington, 260,160,000 cubic kilometers.

In order to determine the volume of the sedimentaries these figures require two small corrections. First, a deduction must be made for the soda, potash, lime and magnesia lost during erosion, and now represented by the corresponding radicles in the ocean. Secondly, for the difference in density between the original rocks and the sedimentaries, indicated by the ratios 2.737:2.6. The first correction is approximately $24,095 \times 10^{12}$ metric tons, or 8,803,000cubic kilometers. Making the corrections, we have, for the actual volume of the sedimentaries,

Survey, 326,590,000 cubic kilometers, or 78,338,000 cubic miles.

Washington, 264,600,000 cubic kilometers, or 63,481,000 cubic miles.

The higher of these figures is equivalent to a shell of rock completely enveloping the earth, 2,100 feet thick, or covering the land area to the depth of 7,198 feet. This estimate is probably a maximum, but it gives fairly well the order of magnitude of the volume to be determined. An exact estimate is of course unattainable, but the total volume of the sedimentary rocks cannot much exceed 80,-000,000 of cubic miles, or roughly, one fourth the volume of the ocean. If we apportion the volume actually found between the different classes of the sedimentaries their volumes in cubic miles become:

Shales																	62,662,400
Sandstones					• •												11,749,200
Limestones	•		 •		• •		•		• •			•	•••		• •		3,916,400
																	78,328,000

This leads to the surprising conclusion that the volume of the limestones is less than that of the oceanic salts, or at least is a quantity of the same order of magnitude. If the fundamental igneous rock was more largely basaltic than the average analyses show, the proportion of limestone would be increased, but probably not to any very great extent. Some allowance should be made for sodium salts enclosed within the rocks; but it is easy to show that such a correction must be small. If all the sandstones had an average porosity of 20 per cent., and if its pore space, once saturated with sea water, retained all of its sodium, the total amount retained would be 110×10^{12} metric tons. This amount, which is evidently excessive, is only 0.75 per cent. of the sodium in the ocean. Its inclusion in the foregoing computations would raise the volume of rock decomposed to 78,100,000 cubic miles, an increase smaller than the unavoidable uncertainties of the computation.

The foregoing estimate of the volume of the sediments obviously includes those which cover a great part of the ocean floor, as well as those which are now on land. Some of the latter, indeed, were once oceanic deposits, and are now, by erosion, being partially returned to the sea, either mechanically as salt and sand, or dissolved in the water of rivers. An exact knowledge of the chemical work of river water is therefore of great statistical importance from several points

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of view. In a former memoir¹¹ I have given a careful estimate of the composition of river waters, and of their entire dissolved load. This estimate is reproduced in the following table: Column I. gives the average composition of the inorganic matter carried in solution by rivers. In column II. the annual contribution of each radicle to the ocean is stated in metric tons.

a subscript the state of the	I. Per Cent.	II Metric Tons per Annum.
CO ₃	35.15	961,350,000
SO4	12.14	332,030,000
C1	5.68	155,350,000
NO ₃	90	24,614,000
Ca	20.39	557,670,000
Mg	3.41	93,264,000
Na	6.40	175,040,000
К	I.5I	41,299.000
(Al, Fe) ₂ O ₃	2.75	75,213,000
SiO ₂	11.67	319,170,000
	100.00	2,735,000,000

The figures in the second column represent the quantity of inorganic matter annually removed from 40,000,000 square miles of the earth's surface, the remaining area being, so far as additions to the ocean are concerned, practically negligible. Interior deserts, closed basins, and the circumpolar lands are left out of account. From 40,000,000 square miles of land, 2,735,000,000 tons of dissolved matter are carried each year to the sea. This quantity, however, is not a true measure of chemical denudation. The NO₃ is of atmospheric origin or else derived from organic sources, and 8 per cent. of the CO₂ represents recent accessions from the atmosphere. Much of the latter radicle is accounted for by the solution of limestones, and was once, of course, atmospheric, but it is now a part of the present erosion. Making the indicated deductions the total quantity of matter transported in solution is reduced to 2,495,585,000 tons annually; or 25×10^8 in round numbers. This, with a probable specific gravity of 2.6 has a volume of 0.96154 cubic kilometer, equivalent to a layer 0.000009281 meter deep, or 0.0003655 inch over the 40,000,000 square miles of land. At this rate the mean

¹¹ A preliminary study of chemical denudation. Smithsonian Misc. Coll., Vol. 56, No. 5, 1910.

surface of the continents would be lowered by solvent erosion alone, to the extent of one foot in 32,833 years. In some areas the rate is much more rapid, in others it is slower; but the average is as close as can be computed with the data now in hand. Its uncertainty may be as great as ten per cent., or perhaps even greater. The chief uncertainty is due to our lack of precise knowledge concerning the greater African and Asiatic rivers.

From the ratio between fluviatile and marine sodium the age of the ocean can be calculated. The ocean contains $14,611 \times 10^{12}$ metric tons of sodium, and the rivers contribute 175,040,000 tons annually. Hence, if the ocean were originally fresh, its entire content of sodium would be supplied by the rivers in 83,472,000 years. This form of calculation was first applied by Joly,¹² whose work is well known; and has since been discussed by Sollas¹³ and also by myself in the memoir already cited. The quotient thus obtained, however, is subject to various corrections, which have been considered by the authors named above, and which operate in opposite directions. Whether they compensate or not it is impossible to say. The calculation, so far, assumes a uniform rate of supply since the surface of the earth took on its present form, and that assumption has been well criticized by Becker.¹⁴ He shows that in all probability the rate is diminishing, for the reason that the exposure of fresh rocks, of unleached material, is constantly growing less and less, and the true age of the earth since stability was established, lies between 55 and 70 millions of years. The higher of these values appears to be the more probable. If, however, the ocean were primitively saline, the quotient representing its age would be still smaller.

Sodium tends to accumulate in the ocean, while the other saline radicles added to it are more or less precipitated as solid deposits on its floor. Calcium and magnesium are removed as carbonates, silica goes to build the skeletons of radiolarians, diatoms, and so forth; potassium is taken to produce glauconite, etc. These deposits or sediments cover vast areas to an unknown thickness, but their

¹³ Quar. Journ. Geol. Soc., Vol. 65, p. xli.

¹⁴ Smithsonian Misc. Coll., Vol. 56, No. 6.

¹² Trans. Roy. Soc. Dublin (2), Vol. 7, p. 23; Rep. British Assoc. Adv. Sci., 1900, p. 369.

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annual increment can be approximately determined. If, from the yearly contributions of rivers the amount of each radicle remaining in solution is subtracted, the rate of chemical sedimentation becomes known. In order to make this calculation, the age of the ocean must be assumed; but variations in the latter estimate affect the results but little. For example, the ocean contains 571.7×10^{12} tons of dissolved calcium, which, divided by the age, gives the annual addition. If the age of the ocean is 100,000,000 years the annual increment of calcium in solution is 5,717,000 tons; if only 50,000,000 years it is 11,434,000 tons. Subtracting these quantities from the total calcium of the river waters the remainders become 551,953,000 and 546,236,000 tons respectively, the difference being much less than the uncertainties in the data employed. If, for the sake of uniformity, we take the uncorrected age of the ocean, 83,472,000 years, the chemical or biotic sediments are represented by the following annual quantities.

SO4	288,021,000 metric tons.
Ca	550,821,000 metric tons.
Mg	71,951,000 metric tons.
К	34,971,000 metric tons.
(Al, Fe) ₂ O ₃	75,213,000 metric tons.
SiO ₂	319,170,000 metric tons.

These are the quantities of the several substances annually removed from solution in the ocean, which, in combination assume the following form.

CaCO ₃	1,347,440,000	metric	tons.
CaSO ₄ .2H ₂ O	50,936,000	metric	tons.
MgCO ₃	251,830,000	metric	tons.
K ₂ SiO ₃	69,045,000	metric	tons.
Limonite	87,905,000	metric	tons.
Silica	295,096,000	metric	tons.
Total	2,104,252,000	metric	tons.

The last group of figures needs some explanation. From the analyses of oceanic sediments published in the reports of the Challenger Expedition I find that the ratio between sulphate calcium and carbonate calcium is 1:45.5. Calcium, therefore, is apportioned between the two salts in that ratio, but much of the SO₄ radicle is left

unaccounted for. Part of it goes to form pyrite, and part is decomposed by organic agencies and lost, but the proportion of loss is unknown. It is, doubtless, large. The potassium which is taken up by clays or else in glauconite is in either instance represented as silicate, and hence a part of the silica is regarded as in combination. The sesquioxides are calculated as limonite, although a part of them is certainly alumina; but no refinement of a calculation here would change the order of magnitude as given. The several orders of magnitude are probably close to the truth, and we may say with much confidence that the precipitates, including such substances as coral, shell, diatomaceous ooze and what not are formed at a rate of something like 21×10^8 metric tons a year, plus a small but undefined allowance for that part of the sulphur which has been fixed as pyrite.

At the figure given, chemical sediments are now forming in the ocean sufficient to cover 88,000,000 square miles of the sea floor to the depth of 0.0001337 inch annually. The whole area of the ocean is 139,440,000 square miles, but the portion covered by the red clay, where the precipitation is relatively insignificant, must be deducted. If the rate had been uniform throughout geological time, 83,472,000 years these sediments would form a layer about 930 feet deep, but such a calculation is unsound. Large areas of what were once marine sediments are now land, and, moreover, neither the rate nor the distribution of the deposits can have been uniform. The limestones that are forming now are largely derived from the solution of older deposits, Cambrian, Silurian, Devonian, Cretaceous, etc., and their carbonates have been deposited in the ocean, not once only, but possibly several times. In the earliest geologic eras, when sediments began to form, the proportion of carbonates to other salts thrown down must have been much smaller than today. An average thickness of 930 feet over the assumed area is therefore a great exaggeration; and needs to be reduced.

It is probably impossible to determine, with any approach to precision, the actual quantity of marine sediments that have been formed. We can, however, make a plausible estimate, which shall, at least, give us some conception of their order of magnitude. It has

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already been shown that the limestones, which are mostly of marine origin, have a volume of 3,916,400 cubic miles. With a specific gravity of 2.7 their mass becomes $42,092 \times 10^{12}$ metric tons. From the figures given on p. 230 ante, the calcareous and magnesian sediments are now forming at a rate bearing a certain ratio to that of the other deposits, the limonitic and siliceous residues. This ratio, which is roundly 1,650:452, if constant throughout geologic time, would give for the latter class of sediments, proportional to the limestones, a mass of 11,664 \times 10¹² tons; the sum of both classes of precipitates being $53,756 \times 10^{12}$ tons. The corresponding average thickness over the sedimentary oceanic area would then be 287 feet. or less than one third of the figure previously given. The actual thickness, however, must be much less; for a large part of the once marine sediments are now elevated into land. According to the best estimates,15 the land area of the globe is now covered by 23 per cent. of archæan and eruptive rocks, and 77 per cent. of sedimentaries. Adding this sedimentary area to that of the ocean, the total becomes 132,180,000 square miles, and the average thickness of the chemical sediments reduces to 191 feet. At the crude value assigned to geologic time this represents a rate of deposition of only 0.000027 inch annually. If the age of the earth is less than 83,472,000 years, the mean annual rate of deposition will be proportionately increased, but not to anything like the present magnitude.

Whether the ratio assumed between the calcareous and siliceous sediments is justifiable or not, is a question admitting of argument. It seems, however, probable, that in the earliest geologic ages, when the land area was occupied principally by igneous rocks, the salinity of the rivers was relatively low, but the proportion of silica to lime in the waters was higher. This suspicion is justified by a study of the river waters of today, especially those issuing from granitoid areas. In such waters silica is often in excess of lime, while in waters from sedimentary areas the reverse is commonly true. The ratio here assumed represents a balancing between waters of both classes, and is therefore as legitimate as any other which might be chosen. Here it must be borne in mind that we are dealing with probabilities only, nothing more.

¹⁵ Von Tillo as modified by Becker. See Becker's memoir already cited.

So far, the mechanical sediments, such as silt and sand, have not been considered. From the surface of the United States, according to Dole and Stabler,¹⁶ the rivers annually carry to the sea 270,-000,000 tons of dissolved substances, and 513,000,000 tons in suspension. If this ratio, which is only approximate, should hold for the whole world, the quantity deposited in the ocean during geologic time would be $102,370 \times 10^{12}$ tons, and the total sedimentation, chemical and mechanical, becomes $156,126 \times 10^{12}$ tons. This quantity, distributed over the entire sedimentary area, continental and oceanic, gives an average thickness of about 550 feet, or 0.000079 inch a year.

The total volume of the marine sediments thus computed, is 13,873,000 cubic miles. The volume remaining in the ocean is very nearly two thirds of this figure, 9,239,000 cubic miles. The volume of all the secondary rocks derived from the decomposition of igneous rocks was previously found to be 78,338,000 cubic miles. Hence the portion now on the land area of the globe amounts to 69,099,000 cubic miles of rock, consisting in great part of materials which were never transported very far from their original place of formation.

To the foregoing estimates of the oceanic sediments at least one large but undetermined correction needs to be applied. The ocean receives great quantities of dust, representative of aerial erosion, and also quantities of volcanic ejectamenta. For these nonfluviatile additions no valid estimates can yet be made. The major portion of them, however, must come from disintegrated sedimentary rocks, sands, and soils, and so do not affect to any serious extent our estimates of rock decomposition. The oceanic share of the sediments should be increased, but less than appears at a first glance. The marine sediments now on land must include a part of the contributions made to the ocean by atmospheric transportation. The actual distribution of the sediments is naturally very uneven. They are probably thin near the margin of the red clay, and thick along the continental shelves. Coral rock, for example, has been bored to a depth of 1,100 feet without reaching its limit. The mechanical sediments are of course mainly deposited relatively near to shore.

¹⁸ U. S. Geol. Surv. Water Supply Paper, No. 234, p. 83.

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In order to prevent misapprehension it may be well to reiterate the statement that these estimates of the marine sediments are necessarily crude, and represent orders of magnitude only. With better evidence, better estimates may at some future time be made, but accuracy in them is unattainable. The other figures given, for the composition of the igneous rocks and of the ocean are probably near the truth but are still subject to revision and improvement.



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