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THE OCCURRENCE OF ELEMENTS IN THE SEA WATER AND IN THE EARTH'S CRUST IN RELATION TO THE PERIODIC SYSTEM OF ELEMENTS

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THE OCCURRENCE OF ELEMENTS IN THE SEA WATER AND IN THE EARTH'S CRUST

in Relation to the Periodic Sistem of Elements

(With 20 Graphs)

by

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INTRODUCTION

The sea water is, in its predominant part, an aqueous solution of various salts. The principal ions already determined in the sea water are *Cl* and *Na*, and, besides them, the other major constituents, *S, Br, Ca, K,* and *Mg*. In addition to these, further elements are being detected, already known to exist in the earth's crust, but, owing to the very low concentrations at which they occur in the sea water, their presence there was not earlier determined. These latter are the so called minor constituents.

It is difficult to draw a sharp division line between those two groups of elements. While G. O. Boguslawsky and O. Krümmel (1907, page 218) were quoting *Cl, Br, S, K, Na, Ca* and *Mg*, besides O and *H,* as the principal elements, H. W. Harvey (1928) included also *C,* and H. W. Harvey (1945) and H. V. Sverdrup, M. W. Johnson, & R. H. Fleming (1946) added *F, B,* and *Sr* to the list.

It is evident now that the existing division into major and minor constituents is a rather artificial one, and that the boundary between the two groups is moving steadily with the extension of knowledge regarding the functions of single elements occurring in sea water.

By using gramatoms instead of grams to express the quantity of elements, we arrive to the conclusion that atoms of *Si* occur in sea water in the same if not in larger quantity than *Sr,* the latter ranking otherwise among the major constituents appearing in sea water. (*Si* 1, 4 x 10^{-1} gramatoms per ton of sea water, and, in the Antartic, 2.5 x 10^{-1} gramatoms p/t, whereas *Sr* 1.5 x 10^{-1} gramatoms p/t).

It is necessary to point out that the reciprocal proportion between the principal elements occurring in the sea water is quite stable in the oceans and in the mediterranean seas, with the exception of a few peripheric seas showing the diluting effect of continental streams (bottlenecked by straits which are slowing down the process of mixing) with smaller or greater differences in ratios of ions, the Baltic Sea being an example.

This rule of stability of reciprocal proportions of ions does not, naturally, apply neither to the inland seas — the Caspian Sea, the Sea of Aral, the Dead Sea, and the like — nor to the salt lakes. Sea water does, therefore, show little if any variability of the percentual composition of its various components and practically does vary only the salinity or the sum total of all salts in 1 kilogram of sea water. The average salinity of ocean water is about $35^{0}/_{00}$.

Is it now possible to fix some regularity, order, or rule, according to which all these constituents occur in the sea water? What is the attitude of contemporary geochemistry and oceanographic science in this respect?

We are acquainted with the rule of homogenity of the composition of the ocean waters, but there is no explanation for the reciprocal ratios between the elements in the sea water.

Sverdrup, Johnson, and Fleming (op. cit.) claim that certain factors are engaged in controlling concentrations of every occurring matter in the sea water. These factors are solubility, physical and chemical reactions and biological activity. The authors add further that our present knowledge is unable to explain what process (or, to be more precise, what processes) are at work in controlling the concentrations of the elements occurring in the sea water.

The chemical composition of the sea water with all the elements hitherto determined, is given in Table 1, showing the elements arranged quantitatively according to their occurrence in the sea water.

This list of elements (Table 1) does not, however, suggest any system or rule, and, indeed, the elements can only be grouped as above, the first group ending with strontium or boron, and the second group comprising the elements occurring in smaller quantities.

Table 1

ELEMENTS OCCURRING IN THE SEA WATER

Element	Symbol	gr/ton	Remark
Chlorine	Cl	18.980	
Sodium (Natrium)	Na	10.561	
Magnesium	Mg	1.272	
Sulphur	S	884	
Calcium	Ca	400	
Potassium (Kalium)	K	380	
Bromine	Br	65	
Carbon	C	28	
Strontium	Sr	13	
Boron	B	4,6	
Silicon	Si	0,02–4.0	
		7.0	1)
Fluorine	F	1.4	
Nitrogen	N	0.01—0.7	
Aluminium	Al	0.5	
Lithium	Li	0.1	2
Rubidium	Rb	0.02	3)
Phosphorus	P	0.001 –0.1	
Barium	Ba	0.L	
Iodine	J	0.Γ	
Arsenic	As	0.01 –0.02	
Iron (Ferrum)	Fe	0.002—0.02	
Manganese	Mn	0.001—0.01	
Copper (Cuprum)	Cu	0.001—0.01	
Zinc	Zn	0.005	
Lead (Plumbum)	Pb	0.004	
Selenium	Se	0.004	
Tin (Stannum)	Sn	0.003	4)
Caesium	Cs	0.002	
Uranium	U	0.0015	
Thorium	Th	0·0005	
Molybdenum	Mo	0.0005	
Gallium	Ga	0.0005	4)
Cerium	Ce	0.0004	
Silver (Argentum)	Ag	0.0003	
Yttrium	Yt	0.0003	
Lanthanum	La	0,0003	
Vanadium	Va	0.0003	
Bismuth	Bi	0 0002	4)
Nickel	Ni	0.0001	
Cobalt	Co	0.0001	4)
Scandium	Sc	0.00004	
Mercury (Hydrargirum)	Hg	0.00003	
Gold (Aurum)	Au	0.000006	
Radium	Ra	0,3 — 3,0 $\times 10^{-10}$	

L05
Γ05

1) *In the Antarctic* (*H. W. Harvey 1945.*)
2) *Thomas & Thompson 1933.* (*Harvey 1945.*)
3) *Wattemberg 1938.* (*Harvey op. cit.*)
4) *Noddack 1940.* (*Harvey op. cit.*)

The latter group, i. e. the minor constituents, is but little investigated and known, with the exception of a few elements to which an important biological function is being attributed (e. g. *N, P, Si,* etc.).

The considerable number of elements known to exist in the sea water renders the orientation among them rather difficult, particularly with regard to their quantitative proportions.

A NEW CRITERION FOR REVIEWING THE ELEMENTS OCCURRING IN THE SEA WATER: THE ATOMIC NUMBER (Z)

The purpose of this paper is not to supply a picture of the elements arranged according to their quantitative occurrence, but to arrange them according to their atomic number.

When composing such a list, we noticed some agreement between the decrease of occurrence and the increase of the atomic number of different elements, resembling to similar properties of the earth's crust (Eggert-Hoçk, 1947).

The author's interest in an arrangement of this kind was aroused by the fact that no such arrangement was to be found in the literature. The well-known specialist for geochemistry, V. M. Goldschmidt (1934), for example, whilst dividing our Earth into atmosphere, hydrosphere, lithosphere, chalcosphere and siderosphere, gives many details dealing with the litho-and chalchospheres, producing also a diagram to illustrate the occurrence of elements in the earth's crust, another diagram showing details relative to the atmospheres of the sun, of the stars, and of the meteors, but only a general survey referring to the hydrosphere, with no diagram at all.

A. P. Vinogradoff (1938), giving the chemical composition of the sea water, does not present a graphic survey for it as he does in the cases of the earth's crust and of organisms.

Eggert-Hock (1947) also, quoting in several places V. M. Golschmidt's works (also the latest ones) and reproducing his data on the occurrence of elements in volcanic rocks and in meteors, does not supply data relative to the sea water.

It seems the more remarkable that not even the latest treatises, dealing particularly with the chemistry of sea water,

Table 2

Atomic Number-Z	Symbol and atomic weight		SEA WATER		EARTH'S CRUST	
			grams per ton	gramatoms per ton	% of weight	% / atom. weight
1	H	1,008	$1,08 \times 10^{5}$	$1,07 \times 10^{5}$	1,00	$1,0 \times 10^{0}$
2	He	4,003	$9,18 \times 10^{-6}$	$2,30 \times 10^{-6}$	$1,0 \times 10^{-6}$	$2,5 \times 10^{-7}$
3	Li	6,940	$1,0 \times 10^{-1}$	$1,44 \times 10^{-2}$	$5,0 \times 10^{-3}$ $6,5 \times 10^{-3}$	$7,2 \times 10^{-4}$ $9,4 \times 10^{-4}$ G.
4	Be	9,02	—	—	$4,0 \times 10^{-4}$ $6,0 \times 10^{-4}$	$4,4 \times 10^{-5}$ $6,6 \times 10^{-5}$ G.
5	B	10,820	$4,6 \times 10^{0}$	$4,26 \times 10^{-1}$	$5,0 \times 10^{-3}$ $3,0 \times 10^{-4}$	$5,0 \times 10^{-4}$ $2,8 \times 10^{-4}$ G.
6	C	12,010	$2,8 \times 10^{1}$	$2,34 \times 10^{0}$	0,35	$2,9 \times 10^{-2}$
7	N	10,008	$7,0 \times 10^{-1}$	$5,0 \times 10^{-2}$	0,04	$2,85 \times 10^{-3}$
8	O	16,000	$8,57 \times 10^{5}$	$6,1 \times 10^{4}$	49,13	$3,07 \times 10^{0}$
9	F	19,000	$1,4 \times 10^{0}$	$7,0 \times 10^{-2}$	0,08 0,027	$4,2 \times 10^{-3}$ $1,4 \times 10^{-3}$ G.
10	Ne	20,183	$2,78 \times 10^{-4}$	$1,38 \times 10^{-5}$	$5,0 \times 10^{-7}$	$2,5 \times 10^{-8}$
11	Na	22,997	$1,05 \times 10^{4}$	$4,57 \times 10^{2}$	2,40 2,83	$1,04 \times 10^{-1}$ $1,23 \times 10^{-1}$ G.
12	Mg	24,320	$1,27 \times 10^{3}$	$5,3 \times 10^{1}$	2,35 2,10	$9,6 \times 10^{-2}$ $8,6 \times 10^{-2}$ G.
13	Al	26,970	$5,0 \times 10^{-1}$	$2,0 \times 10^{-2}$	7,45 8,82	$2;76 \times 10^{-1}$ $3,26 \times 10^{-1}$ G.
14	Si	28,060	$4,0 \times 10^{0}$	$1,4 \times 10^{-1}$	26,00	$9,3 \times 10^{-1}$
15	P	30,980	$1,0 \times 10^{-1}$	$3,0 \times 10^{-3}$	0,2 0,078	$6,4 \times 10^{-3}$ $2,5 \times 10^{-3}$ G.
16	S	32,060	$9,0 \times 10^{2}$	$2,83 \times 10^{1}$	0,1 0,05	$3,1 \times 10^{-3}$ $1,5 \times 10^{-3}$ G.
17	Cl	35,457	$1,9 \times 10^{4}$	$5,48 \times 10^{2}$	0,20 0,048	$5,65 \times 10^{-3}$ $1,35 \times 10^{-3}$ G.
18	Ar	39,944	$6,1 \times 10^{-1}$	$1,50 \times 10^{-2}$	$4,0 \times 10^{-4}$	$1,0 \times 10^{-5}$
19	K	39,096	$3,8 \times 10^{2}$	$9,96 \times 10^{0}$	2,35 2,59	$6,0 \times 10^{-2}$ $6,6 \times 10^{-2}$ G.
20	Ca	40,080	$4,0 \times 10^{2}$	$1,02 \times 10^{1}$	3,25 3,63	$8,1 \times 10^{-2}$ $9,0 \times 10^{-2}$ G,
21	Sc	45,100	$4,0 \times 10^{-5}$	$9,0 \times 10^{-7}$	$6,0 \times 10^{-4}$	$1,3 \times 10^{-5}$
22	Ti	47,900	—	—	0,61	$1,26 \times 10^{-2}$
23	V	50,950	$3,0 \times 10^{-4}$	$6,0 \times 10^{-6}$	0,02 0,01	$4,00 \times 10^{-4}$ $2,0 \times 10^{-4}$ G.
24	Cr	52,010	—	—	0,03	$5,7 \times 10^{-4}$
25	Mn	54,930	$1,0 \times 10^{-2}$	$1,9 \times 10^{-4}$	0,1	$1,85 \times 10^{-3}$
26	Fe	55,850	$2,0 \times 10^{-2}$	$3,6 \times 10^{-4}$	4,20 5,1	$7,4 \times 10^{-2}$ $9,1 \times 10^{-2}$ G.
27	Co	58,940	$1,0 \times 10^{-4}$	$2,0 \times 10^{-6}$	$2,0 \times 10^{-3}$ $4,0 \times 10^{-3}$	$3,4 \times 10^{-5}$ $6,8 \times 10^{-5}$ G.
28	Ni	58,690	$1,0 \times 10^{-4}$	$2,0 \times 10^{-6}$	0,02 0,01	$3,41 \times 10^{-4}$ $1,7 \times 10^{-4}$ G.
29	Cu	63,570	$1,0 \times 10^{-2}$	$1,57 \times 10^{-4}$	0,b	$1,55 \times 10^{-4}$
30	Zn	65,380	$5,0 \times 10^{-3}$	$8,0 \times 10^{-5}$	0,02 0,004	$3,05 \times 10^{-4}$ $6,0 \times 10^{-5}$ G.
31	Ga	69,720	$5,0 \times 10^{-4}$	$7,2 \times 10^{-6}$	$1,0 \times 10^{-4}$ $1,5 \times 10^{-3}$	$1,43 \times 10^{-6}$ $2,2 \times 10^{-5}$ G.
32	Ge	72,600	—	—	$1,0 \times 10^{-4}$ $7,0 \times 10^{-4}$	$1,38 \times 10^{-6}$ $9,6 \times 10^{-6}$ G.
33	As	74,910	$2,0 \times 10^{-2}$	$3,0 \times 10^{-4}$	$5,0 \times 10^{-4}$	$6,6 \times 10^{-6}$
34	Se	78,960	$4,0 \times 10^{-3}$	$5,0 \times 10^{-5}$	8.0×10^{-5} $6,0 \times 10^{-5}$	$1,0 \times 10^{-6}$ $7,6 \times 10^{-7}$ G.
35	Br	79,916	$6,5 \times 10^{1}$	$8,3 \times 10^{-1}$	$1,1 \times 10^{-3}$	1.25×10^{-5}
36	Kr	83,70	$3,1 \times 10^{-4}$	$3,7 \times 10^{-6}$	$1,0 \times 10^{-3}$	$1,18 \times 10^{-5}$
37	Rb	85,48	$2,0 \times 10^{-2}$	$2,35 \times 10^{-4}$	0,03	$3,51 \times 10^{-5}$
38	Sr	87,63	1.3×10^{1}	$1,47 \times 10^{-1}$	0,035	$4,0 \times 10^{-4}$
39	Y	88,92	$3,0 \times 10^{-4}$	$3,0 \times 10^{-6}$	$5,0 \times 10^{-3}$ $3,1 \times 10^{-3}$	$5,6 \times 10^{-5}$ $3,3 \times 10^{-5}$ G.
40	Zr	91,22	—	—	0,025	$2,7 \times 10^{-4}$

L01

L4

Table 2 (continued)

Atomic Number-Z	Symbol and atomic weight		SEA WATER		EARTH'S CRUST	
			grams per ton	gramatoms per ton	% of weight	% / atom. weight
41	Nb	92,91	—	—	3,2 $\times 10^{-5}$	3,44 $\times 10^{-7}$
					1,5 $\times 10^{-3}$	1,6 $\times 10^{-5}$ G.
42	Mo	95,95	7,0 $\times 10^{-4}$	7,3 $\times 10^{-6}$	1,0 $\times 10^{-3}$	1,04 $\times 10^{-5}$
43	Tc(Ma)	98,913	—	—	1,0 $\times 10^{-7}$	1,0 $\times 10^{-9}$
44	Ru	101,70	—	—	5,0 $\times 10^{-6}$	5,0 $\times 10^{-8}$
45	Rh	102,91	—	—	1,0 $\times 10^{-6}$	1,0 $\times 10^{-8}$
					1,0 $\times 10^{-7}$	1,0 $\times 10^{-9}$ G.
46	Pd	106,70	—	—	5,0 $\times 10^{-6}$	4,7 $\times 10^{-8}$
					1,0 $\times 10^{-6}$	1,0 $\times 10^{-8}$ G.
47	Ag	107,880	3,0 $\times 10^{-4}$	3,0 $\times 10^{-6}$	1,0 $\times 10^{-5}$	9,2 $\times 10^{-8}$
48	Cd	112,41	—	—	5,0 $\times 10^{-4}$	4,4 $\times 10^{-6}$
					5,0 $\times 10^{-5}$	4,4 $\times 10^{-7}$ G.
49	In	114,76	—	—	1,0 $\times 10^{-5}$	8,7 $\times 10^{-8}$
50	Sn	118,70	3,0 $\times 10^{-3}$	3,0 $\times 10^{-5}$	8,0 $\times 10^{-3}$	6,7 $\times 10^{-5}$
					4,0 $\times 10^{-3}$	3,3 $\times 10^{-5}$ G.
51	Sb	121,76	—	—	5,0 $\times 10^{-5}$	4,1 $\times 10^{-7}$
					1,0 $\times 10^{-4}$	8,0 $\times 10^{-7}$ G.
52	Te	127,61	—	—	1,0 $\times 10^{-6}$	7,8 $\times 10^{-9}$
53	J	126,92	5,0 $\times 10^{-2}$	4,0 $\times 10^{-4}$	1,0 $\times 10^{-4}$	7,8 $\times 10^{-7}$
					3,0 $\times 10^{-5}$	2,3 $\times 10^{-7}$ G.
54	X	131,30	1,05 $\times 10^{-4}$	8,0 $\times 10^{-6}$	3,0 $\times 10^{-9}$	2,3 $\times 10^{-11}$
55	Cs	132,91	2,0 $\times 10^{-3}$	2,0 $\times 10^{-5}$	1,0 $\times 10^{-3}$	7,5 $\times 10^{-6}$
					7,0 $\times 10^{-4}$	5,3 $\times 10^{-6}$ G.
56	Ba	137,36	5,0 $\times 10^{-2}$	4,0 $\times 10^{-4}$	0,05	3,6 $\times 10^{-4}$
					0,039	2,8 $\times 10^{-4}$ G.
57	La	138,92	3,0 $\times 10^{-4}$	2,0 $\times 10^{-6}$	1,8 $\times 10^{-3}$	1,3 $\times 10^{-5}$
58	Ce	140,13	4,0 $\times 10^{-4}$	3,0 $\times 10^{-6}$	4,4 $\times 10^{-3}$	3,15 $\times 10^{-5}$
59	Pr	140,92	—	—	5,6 $\times 10^{-4}$	4,0 $\times 10^{-6}$ G.
60	Nd	144,27	—	—	2,4 $\times 10^{-3}$	1,7 $\times 10^{-5}$ G.
61	Il	—	—	—	—	—
62	Sm	150,43	—	—	6,5 $\times 10^{-4}$	4,3 $\times 10^{-6}$ G.
63	Eu	152,00	—	—	1,0 $\times 10^{-4}$	6,5 $\times 10^{-7}$ G.
64	Gd	156,9	—	—	6,3 $\times 10^{-4}$	4,0 $\times 10^{-6}$ G.
65	Tb	159,2	—	—	1,0 $\times 10^{-4}$	6,3 $\times 10^{-7}$ G.
66	Dy	162,46	—	—	4,3 $\times 10^{-4}$	2,6 $\times 10^{-6}$ G.
67	Ho	164,94	—	—	1,2 $\times 10^{-4}$	7,2 $\times 10^{-7}$ G.
68	Er	167,2	—	—	2,4 $\times 10^{-4}$	1,4 $\times 10^{-6}$ G.
69	Tu	169,4	—	—	3,0 $\times 10^{-5}$	1,8 $\times 10^{-7}$ G.
70	Yb	173,04	—	—	2,6 $\times 10^{-4}$	1,5 $\times 10^{-6}$ G.
71	Lu(Cp)	174,99	—	—	7,0 $\times 10^{-5}$	4,0 $\times 10^{-7}$ G.
72	Hf	178,00	—	—	4 0 $\times 10^{-4}$	2,2 $\times 10^{-6}$
					3,2 $\times 10^{-4}$	1,8 $\times 10^{-6}$ G.
73	Ta	180,88	—	—	2,4 $\times 10^{-5}$	1,3 $\times 10^{-7}$
74	W	183,92	—	—	7,0 $\times 10^{-3}$	3,7 $\times 10^{-5}$
75	Re	186,31	—	—	1,0 $\times 10^{-7}$	5,3 $\times 10^{-10}$
76	Os	190,20	—	—	5,0 $\times 10^{-6}$	2,6 $\times 10^{-8}$
77	Ir	193,10	—	—	1,0 $\times 10^{-6}$	5,1 $\times 10^{-9}$
78					1,0 $\times 10^{-7}$	5,1 $\times 10^{-10}$ G.
	Pt	195,23	—	—	2,0 $\times 10^{-5}$	1,02 $\times 10^{-7}$
79					5,0 $\times 10^{-7}$	2,6 $\times 10^{-9}$ G.
	Au	197,20	4,0 $\times 10^{-6}$	2,0 $\times 10^{-8}$	5,0 $\times 10^{-7}$	2,57 $\times 10^{-9}$
80	Hg	200,61	3,0 $\times 10^{-5}$	1,5 $\times 10^{-7}$	5,0 $\times 10^{-5}$	2,5 $\times 10^{-7}$
81	Tl	204,39	—	—	1,0 $\times 10^{-5}$	4,9 $\times 10^{-8}$
82					3,0 $\times 10^{-5}$	1,5 $\times 10^{-7}$ G.
	Pb	207,21	4,0 $\times 10^{-3}$	2,0 $\times 10^{-5}$	1,6 $\times 10^{-3}$	7,7 $\times 10^{-6}$
83	Bi	209,00	2,0 $\times 10^{-4}$	1,0 $\times 10^{-6}$	1,0 $\times 10^{-5}$	4,8 $\times 10^{-8}$
					2,0 $\times 10^{-5}$	1.0 $\times 10^{-7}$ G.
74	Po	210,0	—	—	5,0 $\times 10^{-6}$	2,33 $\times 10^{-8}$
85	At	—	—	—	—	—
86	Rn	222,0	—	—	—	—
87	Fr	—	—	—	—	—
88	Ra	226,05	3,0 $\times 10^{-10}$	1,2 $\times 10^{-12}$	2,0 $\times 10^{-10}$	8,8 $\times 10^{-13}$
89	Ac	—	—	—	—	—
90	Th	232,12	4,0 $\times 10^{-4}$	2,0 $\times 10^{-6}$	1,0 $\times 10^{-3}$	4,3 $\times 10^{-6}$
91	Pa	231,	—	—	7,0 $\times 10^{-11}$	3,0 $\times 10^{-13}$
92	U	238,07	2,0 $\times 10^{-3}$	1,0 $\times 10^{-5}$	4,0 $\times 10^{-4}$	1,68 $\times 10^{-6}$

discuss the available data concerning the diffusion, resp. the occurrence of the elements in the sea water in connection with the sequence of the atomic numbers of elements (Harvey, 1928; Kalle, 1943; Harvey, 1945; Sverdrup- Johnson- Fleming, 1946).

In Table 2, the available data concerning the elements occurring in the sea water are collected. These data derive from four up-to-date oceanographic works. The fourth column shows the quantities of elements (in grams) contained in a ton of sea water whose salinity is $35^{0}/_{00}$. The fifth column consists of data from the previous column, divided by the respective atomic weigt (third column) for the purpose of obtaining the values in gramatoms, these values preventing mistakes that would otherwise be possible. While composing this table, we observed carefully the terms recommended by the L'Association d'Oceanographie Physique (Helland - Hansen, Jacobsen & Thompson, 1948, page 8).

Fig. 1 gives such a picture drawn according to the available data (Table 2), the abcissa being the atomic number of an element, and the ordinate being the logarithm of the number showing how many grams of this element are contained in a ton of sea water, divided by the atomic weight of the element.

The real quantities of weights of particular elements as they occur in the sea water, have been divided by atomic weights in order to obtain in this way more positive data. The gramatom is evidently better suited for the purpose than the gram, because it enables us to obtain the figures illustrating the real numerical ratios between single kinds of atoms, which is not the case if the gram is taken as a unit.

This picture shows clearly that the major constituents are arranged almost in an order among the first elements in the row of the atomic numbers, and that the elements on the right side of the picture occur but in small quantities in the sea water. If the table of the elements by Antropoff (Table 3) is considered, almost all major constituents will be located among the so called head-elements, i. e. elements of the second and third periods of the periodic system of elements.

Graphic surveys of this kind have been given for elements occurring in the earth's crust (Goldschmidt 1934; I. and

Table 3

The Periodic System of Elements as Rearranged by Werner

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	(Tc)	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	X
Cs	Ba	La1)	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	(At)	Rn
(Fr)	Ra	Ac	Th	Pa	U												

1) Rare earths

W. Noddack, and others), based upon analyses and estimations made by Clarke and Washington (1925), V. M. Goldschimdt (1937), Vernadsky (1907), I. and W. Noddack (1934). Departing from spectrographic measurements, estimations have been made of the occurrence of some elements in the atmospheres of the sun and of some other stars. Chemical analyses of the meteorites have contributed to our knowledge regarding the composition of other celestial bodies.

For data relative to the occurrence of elements in the Earth's crust F. Tućan (1928) has been consulted. This author is quoting again Clarke's and Vogt's data for the majority of elements. K. Kalle (1943) and Floroff and Judkevič (1946) have also been found useful. These authors take the data from Fersman's »Geochemistry«. The latter two authors who have the data from Fersman's »Geochemistry« (where all available data given by other authors have been carefully collected), were our principal guide when preparing the big Table 2 (columm 6). It is quite certain that the data given by V. M. Goldschmidt (1937) have also been taken by these authors. As their data, however, markedly differ in some instances, the data taken from Goldschmidt (1937) are designated by a »G«.

V. J. Vernadski (Tućan, 1930) arranged all the elements occurring in the earth's crust in decades, according to their percentual participation in its formation.

To make comparisons possible between the occurrence of the elements in the sea water and in the earth's crust, we followed the same method as has already been applied to the sea water, i. e. we divided the quantities of the elements by their atomic weights (Table 2, column 7). Basing upon these data, the diagram illustrating the occurrence of elements in the earth's crust (Fig. 2) has been drawn, the atomic number of the element representing the abscissa and the ordinate being the exponent of value from column 7 or the logarithm of gramatoms of the element in p. c.

According to Oddo & Harkins, elements of even atomic numbers occur in larger quantities than their uneven neighbours. This fact is plainly visible in the case of rare earths and as far as the elements on the right side of the diagram in general are concerned, whereas data belonging to the left side of the diagram do not comply with this rule, to quote for example the following groups:

Be — *B* — *C* . . . . increasing
O — *F* — *Ne* . . . . . . decreasing
Mg — *Al* — *Si* . . . . . . increasing
Si — *P* — *S* . . . . decreasing
Ar — *K* — *Ca* . . . . . . increasing
V — *Cr* — *Mn* — *Fe* . . increasing
Ge — *As* — *Se* . . . . . decreasing
Kr — *Rb* — *Sr* . . . . . increasing
Rh — *Pd* — *Ag* — *Cd* . . increasing
Sn — *Sb* — *Te* . . . . . decreasing
X — *Cs* — *Ba* . . . . . . increasing

The occurrence of the elements in decreasing quantities with the increase of their atomic number is another observation which has been made earlier already.

This rule has actually only an average value, because the curve (Fig. 2) shows great irregularities, and in many instances there are several elements on the right side of an element whose occurrences are more strongly pronounced than of that element itself. This, therefore, seems to be an imperfect rule (in its very substance, the rule Oddo-Harkins is also partially inconsistent with this rule of decrease of the elements).

Now this is the position regarding the occurrence of the elements in the earth's crust. Having at our disposal the diagram dealing with the conditions in the sea water (Fig. 1),

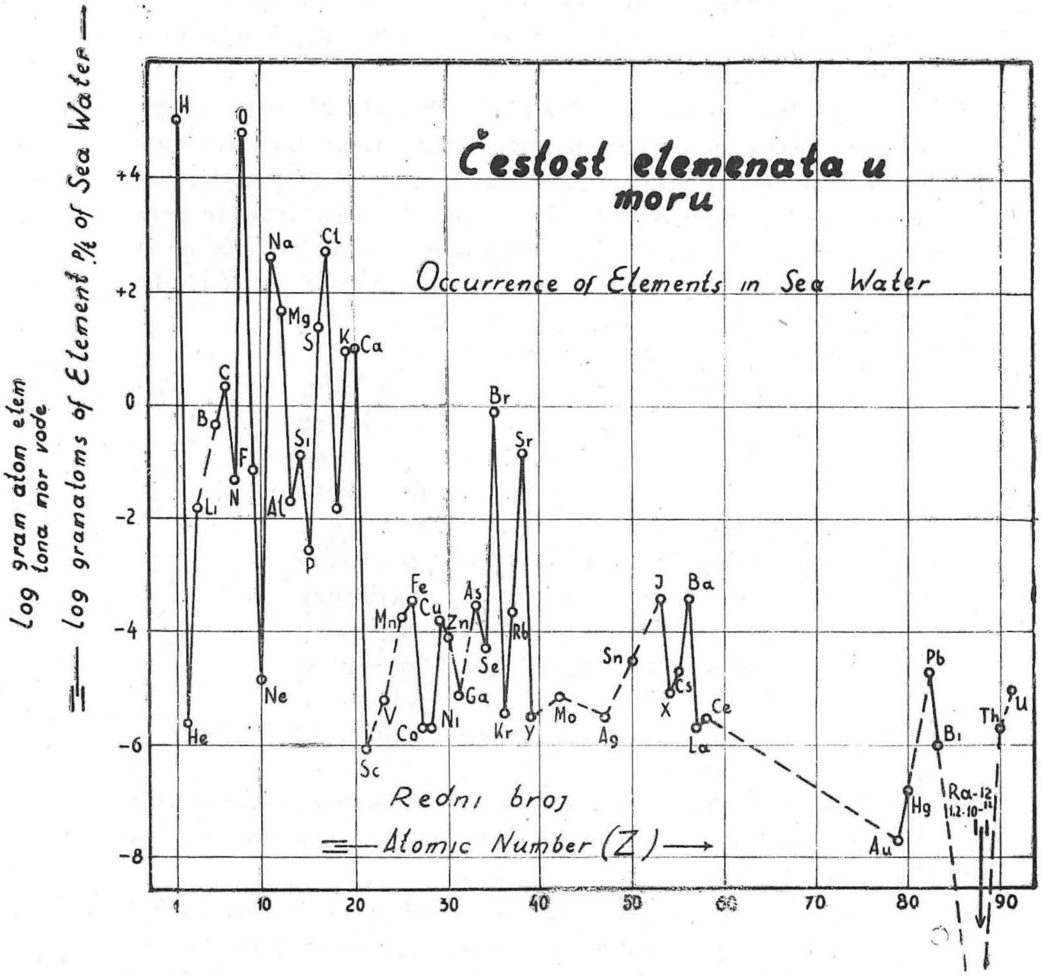


Fig. 1

we are able to observe the facts relative to the occurrence of the elements in it.

It does not require much study to state that the rule of Oddo and Harkins does not apply here, perhaps owing to the fact that many data regarding the conditions in the sea are still

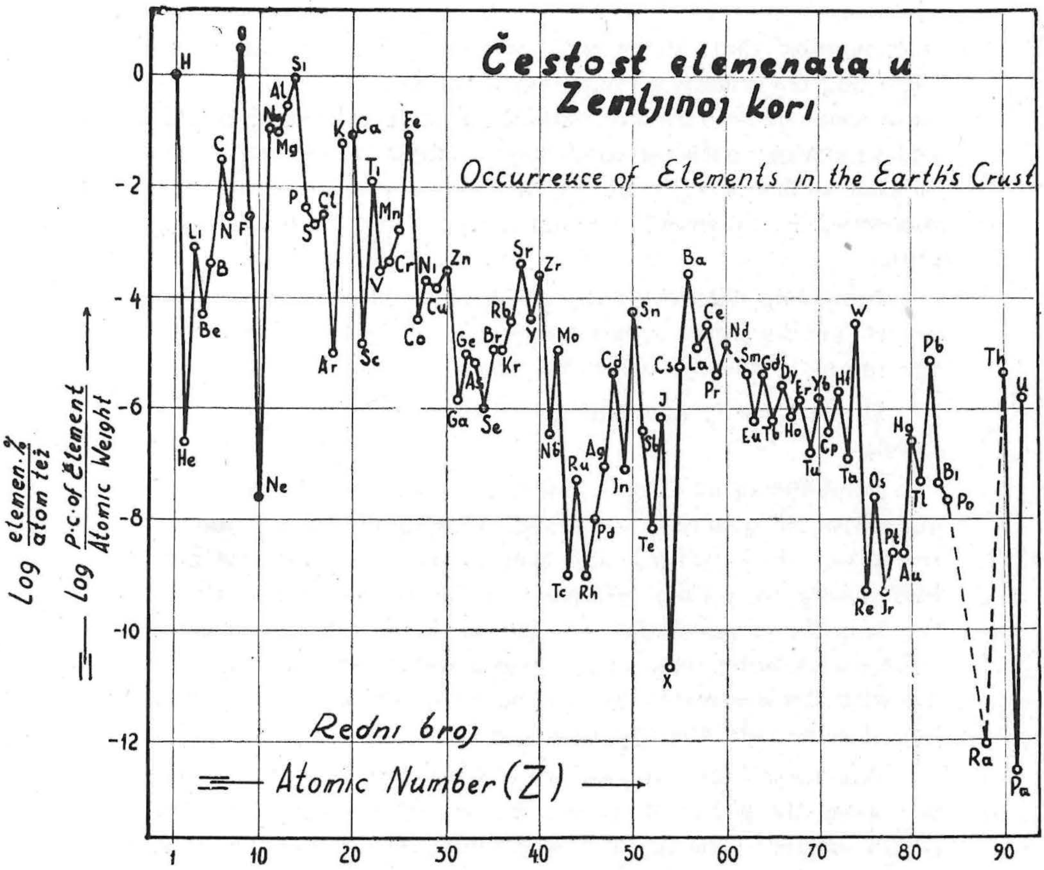


Fig. 2

missing (for about a half of all the elements). But we can already claim quite positively that the following groups are inconsistent with this rule:

O — F — Ne . . . . decreasing
Na — Mg — Al . . . . . decreasing

P — *S* — *Cl* . . . . increasing
Ar — *K* — *Ca* . . . . . . increasing
Fe — *Co* — *Ni* . . . . . . decreasing
Cu — *Zn* — *Ga* . . . . . . decreasing
Kr — *Rb* — *Sr* . . . . . . increasing

It is possible that, along with the completion of information regarding the conditions existing in the sea water, we may disclose some more harmony with the rule of Oddo and Harkins, and an analogy with the conditions existing in the earth's crust, at least as far as elements of the higher atomic numbers are concerned, i. e. elements belonging to the right side of the diagram.

In dealing with this subject, elements have been mentioned as yet undetermined in sea water, but likely to be detected in the course of further observations.

How to justify now this claim, sustained with so much certainity?

Solubility of all matter in distilled water, even if in minimal quantities, is generally supposed. This applies particularly to sea water. Sverdrup and others (op. cit., page 203) assert that, owing to mutual influence of the ions, the activity resp. the capacity of particular ions to join independently in certain reactions is being reduced in the sea water, which, in comparison with distilled water, has the power to dissolve larger quantities of some only slightly soluble salts.

But doesn't this suggest the existence of some other factor increasing the power of the sea water to dissolve larger quantities of matter? This agent is represented by organic matter. Sea water is known to contain the so called humic complexes, and the alcaline salts of humic acids have the property to produce clear water solutions from otherwise insoluble matter.

Noddack and Noddack, 1934 (Eggert-Hock, op. cit.) suppose that in all the minerals small quantities of all elements are present (water being also a mineral!).

Strikingly enough, data have been supplied regarding a number of further elements, whose presence in the sea water were quite unknown earlier, viz.:

Ba	detected	in	1924
Pb	»	»	1930
Zn, V, Mo, Ni	»	»	1936
Ce, Sc, La, Y, Hg	»	»	1937
Se	»	»	1938
Th	»	»	1939
Sn, Ga, Co, Bi	»	»	1940

Although not yet detected in sea water, *Cd* has been found in marine organisms (Webb 1937 — Harvey 1945) and also *Ti, Cr, Cd, Tl,* and *Sb* (Noddack and Noddack, 1940 (op. cit.).

While in 1907 Boguslawsky and Krümmel mentioned 27 elements as contained in sea water, Harvey in 1945 stated 45 elements with further 6 elements determined in marine organisms.

It results quite clearly from these observations that the number of elements contained in sea water is constantly completing thus strengthening the opinion that all chemical elements are contained in the sea water — a fact to be definitely proved sooner or later.

When comparing the two graphs — one illustrating the distribution of elements in the lithosphere (Fig. 2) and the other relative to the elements in the sea water (Fig. 1) — a striking likeness of their general features will be noticed. This fact is the more curious as it relates to two thoroughly different mediums: to the sphere of the earth's crust and to the sphere (envelope) of water.

The first is a world of solid minerals, and the second is a water system of immense dimensions. A true conception of the difference between these two worlds cannot be reached by the mere statement claiming the existence of two systems of different states of aggregation, but also from the fact that the earth's crust consists of all kinds of freely mixed matter of infinite variety, mutually almost quite independent, mutually divided by space, their presence not necessarily influencing each other.

The second is mostly, if not exclusively, a solution of various matter, being, as already said, a homogeneous solution where each component is practically uniformly distributed and everywhere present. Here are different elements in closest vicinity to each other, incessantly influencing each other by their mere presence.

Here the earth's crust — a varied mixture of solid matter, divided by space, and there the sea — a homogeneous solution of matter, closely intermingled in space. Distinctly separated, these two worlds show quite different dominating elements: the first *Si, Al* and *Fe,* the second *H, Cl* and *Na.*

But this is only in appearance so. Our pictures tell us, on the contrary, something quite different, something unexpected, or even surprising. In the same way as our sun, or the distant stars (incandescent gases), according to their chemical composition bear likeness to our earth's solid crust, so the sea is akin to both.

The hydrosphere is, of course, only a part of the Earth, from which it derives and, in the same way as its mineral composition, represents a sort of aqueous extract from the lithosphere and from the onetime atmosphere. The similarity of the occurrence as given above spontaneously suggests this picturesque and daring parallel, which must not be taken literally, this similarity beeing of a quantitative nature only.

Thus we see how the conditions in the sea water, concerning the decrease of occurrence of elements, agree with conditions in the earth's crust. Curves on Pict. 1 and 2, broadly taken, almost coincide. The downward trend is evident. But stress should be put here also upon the fact that this decrease of the occurrence of elements following the increase of their atomic number, has but an approximate value, because it concerns their principal features only, owing to many exceptions, as in the case of the earth's crust.

ANOTHER CRITERION: THE PERIODIC SYSTEM OF ELEMENTS

Influenced by the significance of the atomic numbers — introduced into Physics by Moseley (1913), thus lending the most important characteristic to each of the elements — the geochemists employed this way of exposing the occurence of elements in the earth's crust.

The atomic number apparently determines the properties of the atomic structure of each of the elements, being equal to the number of negatively charged electrons of the outer orbit of the atom, as well as to number of positively charged particles of the nucleus. The atomic number appears, then, to be the reflection of a deeply objective reality which must not be neglected. It is a factor of aperiodicity of the elements. Upon this criterion, then, the above way of exposing the occurrence of the elements is basing.

But besides this monotonous function there is also the momentum of periodicty, pertaining to the elements in general, first noticed by Mendeleeff and several times afterwards brilliantly confirmed and advantageously made use of.

The periodicity of the properties of the elements is also an expression of their atomic structure, particularly of the structure of their eletronic outer orbits. This criterion is also deeply objective, because chemical and some physical properties of a certain atom depend on this structure. This criterion is both interesting and useful in our case.

We noticed how *Cl, Br,* and *J* decrease in a regular way and not without order, as might be judged from observing the picture of all elements as a whole. So we started to arrange the elements occurring in sea water according to groups of the periodic system of elements, obtaining as a result the regularity and the functional connection between the occurrence and the atomic number. When trying to apply this experience to conditions pertaining to the earth's crust, analogous conditions and regularities resulted — a fact which remained hitherto unnoticed, having been concealed by reciprocal relationship of the groups of the periodic system of elements. It was this fact that induced us to observe the occurrence of all the elements, not simultaneously, but separately in groups.

Proceeding along this line the author arrived at observations which will follow on further pages of this study, but which already provide the basis for the statement that exactly the periodical change of the properties of elements in the course of single periods of the system of elements produced an obstacle for a clear review of the occurence of elements, every group of the periodic system having its own regularity and relation between the occurrence and the atomic number. This has been named the Group Rule. There is some restriction, some closeness of elements within the groups, but there is no interdependence of elements of single periods, this being easily perceived by comparing the elements of the second period — from lithium to neon, or from beryllium to argon. This will follow clearly in the further course of this study, but it is already evident that, by comparing the occurrences of all the elements taken together, i. e. the various groups of elements at the same time, we do not get a picture suggesting some regularity of relation between the elements, resp. between their occurrence and the increase of their atomic number.

As already stated, elements of the same group are interdependent, this fact being due to their possessing electronic outer orbits of the same kind. The elements of the group I, for instance, possess the following structure of the two outer electronic orbits:

Head elements	*Li*	2/1
	Na	2,6/1
Subgroup I a . . .	*K, Rb, Cs*	2,6/1
Subgroup I b . . .	*Cu, Ag, Au*	2,6,10/1

As shown above, the head elements and the elements belonging to the subgroup Ia have the same structure of their electronic outer orbits, while the elements of the subgroup Ib differ in some degree. This partial difference of the elements belonging to subgroups »a« and »b« with regard to the structure of their outer orbits, is met in all the groups of the periodic system. This fact suggests the necessity of considering the elements of the subgroup »a« separately, and apart from those of the subgroup »b«. From the group III onwards, the head elements agree with the elements of the subgroup »b« concerning the structure of their outer orbits.

Elements belonging to the same period are, on the contrary, heterogenous in this respect. Let the following review of electronic outer orbits of the second period (L) illustrate this statement:

	Li	*Be*	*B*	*C*	*N*	*O*	*F*	*Ne*
K	2	2	2	2	2	2	2	2
L	1	2	2	2	2	2	2	2
			1	2	3	4	5	6

Their outer orbits differ continually from the first to the last member of the period. When all the elements, regardless of groups, are arranged according to their occurrence, it is just this moment of change that produces a »disturbance« or »disorder« regarding the occurrence of the elements. For this reason this factor of »disturbance« should be removed so as to enable us to limit our observation of the relationship between the decrease of the occurrence of the elements and the increase of their atomic number to homogenous elements only i. e. those arranged in groups.

The Group Rule

By applying this method, we have found, in the course of the preparation of this paper, that such conditions with regard to occurrence of the elements exist both in the sea water and in the earth's crust, thus enabling us to formulate the rule determining that the occurrence of the elements belonging to single groups of the periodic system of elements is a function of their atomic number.

This rule has the validity in the frame of the above formulation only, and, therefore, it has been briefly called »The Group Rule«.

In the course of collecting and examining the material for this paper, much regularity of relations has been found to exist within the investigated material, encouraging us to make certain generalizations, which are expressed by the above rule and by several ones still to follow.

But there are also a few inconsistences with regard to this regularities of the occurrence of elements, that require explanation. One of the possible explanations — thus far the only one at our disposal, and quite acceptable according to our opinion — has it that the former estimates and regulations of occurrence of these few, still inconsistent, elements are defective in some way, and that further investigations will finally produce the solution of these cases and submit also these few elements to the above regularities. It is not to be excluded, however, that some exceptions from the rule may stil remain after the new investigations have been made, and that some other explanation, different from ours, will be necessary. It is in this way that all our anticipations of revisions of actual values of the occurence of the elements in the earth's crust should be understood, as well as our estimates of possible occurrence of elements in the sea water which have not yet been determined there.

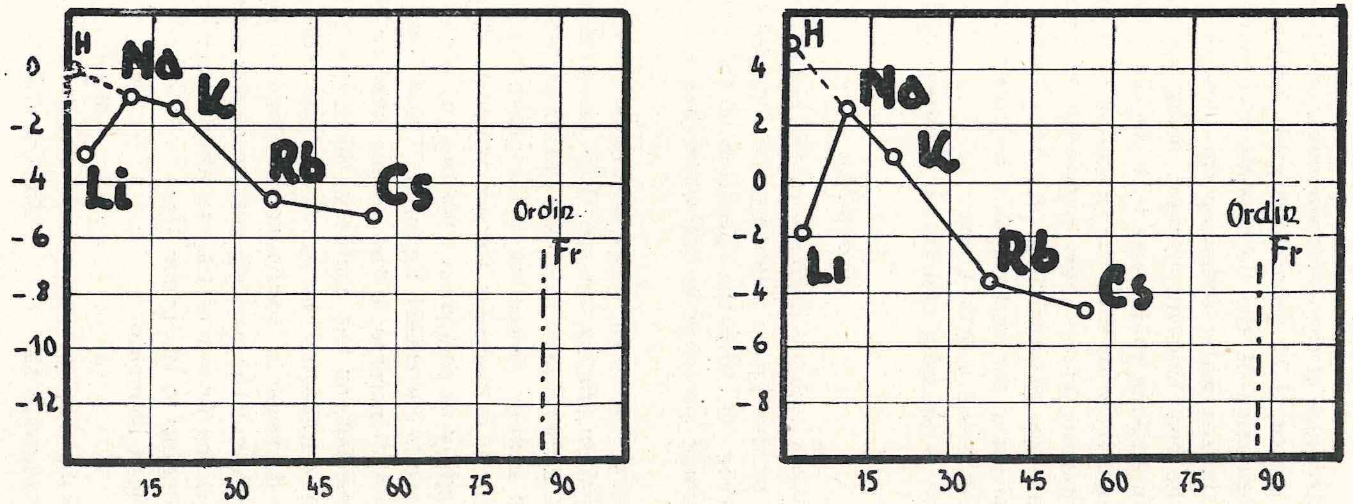
THE SURVEY OF THE OCCURRENCE OF ELEMENTS ACCORDING TO THE GROUPS OF THE PERIODIC SYSTEM OF ELEMENTS

In the figures 3 to 18 the abscissae indicate the atomic number. Numbers on the ordinates (referring to »Earth« and »Sea«) have the same significance as on the figures 1 and 2, from where they are taken from. Figures 3 to 18 have been drawn in a way to make a direct comparison between the data contained in the figures on the left and those on the right side possible.

The designations used for the ordinates concerning the earth's crust on the one hand and the sea water on the other hand, apparently differ between themselves, because the way of expression has been maintained as practised in the geologic and oceanographic literature respectively (% and g/t), so that, actually, e. g. the designation -6 on the ordinate concerning the earth's crust correspondes to -2 on the ordinate belonging to the graph for sea water.

In this manner we see, for instance, from the figure of the I b group, that 1 ton of the earth's crust contains 10.000 times more copper (*Cu*) than it is to be found in 1 ton of sea water. The groups to which these elements belong are placed on top of the graph. The groups of the periodic system of elements are designated in the figures. Black points have been placed according to date taken from Goldschmidt (1937) and white points according to remaining data from Table 2.

GROUP Ia


The Earth's Crust

The Sea Water

Fig. 3

Group I a.

The structure of the electronic outer orbits is given on page 18, while the curve of decrease is given on Fig. 3, showing an evident regularity of the decreasing occurrence of these elements in the sea water following the increase of their atomic number, the head-element, lithium, being an exception. These facts are in striking conformity with the conditions found in the earth's crust, likewise with the exception of lithium.

The decrease shows more regularity in sea water, particularly in the case of potassium *(K)* where some upward deviation in the curve for earth should be noted, the occurrence of this element being a little larger.

(There is an easy connection between hydrogen and the curve).

Group II a

There is a regular decrease of the occurrence of elements belonging to this group following the increase of their atomic numbers (Fig. 4), with the exception of the head-element, beryllium, whose presence in sea water has not yet been determined.

The curve for earth shows analogous conditions. The quantity of beryllum *(Be)* is for over three potencies smaller in comparison with the second head-element, magnesium *(Mg),* (as in the case of lithium, belonging to the group Ia).

The curve of decrease for sea water is otherwise running more straightly as compared with the line for earth, the course of the latter being rather agitated. These lines present a rare case: with the increase of the atomic number we do not get a straight line but, on the contrary, there is a growing decrease of occurrence following the increase of the atomic number. (See also: »the decrease of occurrence of elements belonging to the seventh period of the periodic system of elements«).

Here is the review of the electronic outer orbits of the elements belonging to the group IIa:

Head elements	*Be*	2/2
	Mg	2,6/2
Subgroup IIa	*Ca, Sr, Ba, Ra*	2,6/2
Subgroup IIb	*Zn, Cd, Hg*	2,6,10/2

GROUP IIa

The Earth's Crust

The Sea Water

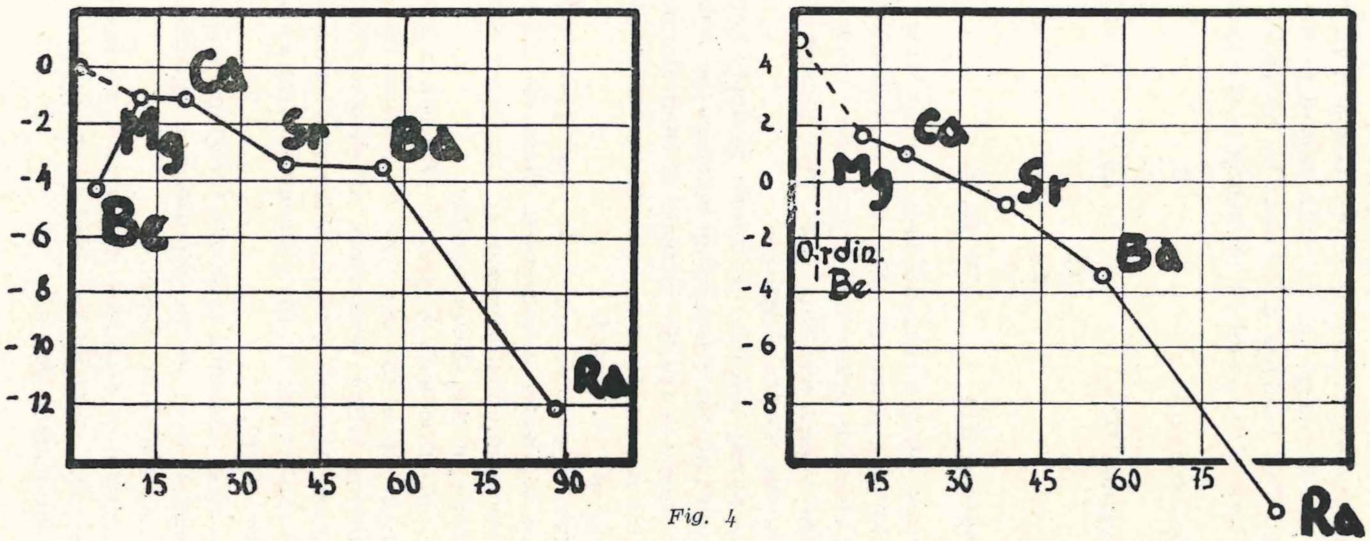


Fig. 4

Subgroup III a

Here the head elements *B* and *Al* depart from the subgroup »a« to join the subgroup »b« with regard to the occurrence of elements. This becomes quite clear by reviewing the electronic outer orbits of the members belonging to the group III:

Head elements	*B*	2/2,1
	Al	2,6/2,1
Subgroup IIIa	*Sc, Y, La, Ce* & 59-71	2,6,1/2
	Th	2,6,2/2
	Pa	2,6,3/2
	U	2,6,5/1
Subgroup IIIb	*Ga, In, Tl*	2,6,10/2,1

In fact, all the elements occur in sea water in nearly like quantities of gramatoms (Fig. 5). — (Comparisons of quantities of elements given in this paper were made possible by applying the values resulting from the division of weights in grams by the atomic weights).

It is hardly possible, therefore, to apply here the previous rule concerning the relationship between the decrease of occurrence of elements and the increase of their atomic number. This is true for sea water at least as far as the known elements of this group are concerned.

Similar conditions appear to exist also in the earth's crust. So far as sea water is concerned, there are cases in this group when even a minimal increase of occurrence takes place with the decrease of the atomic number.

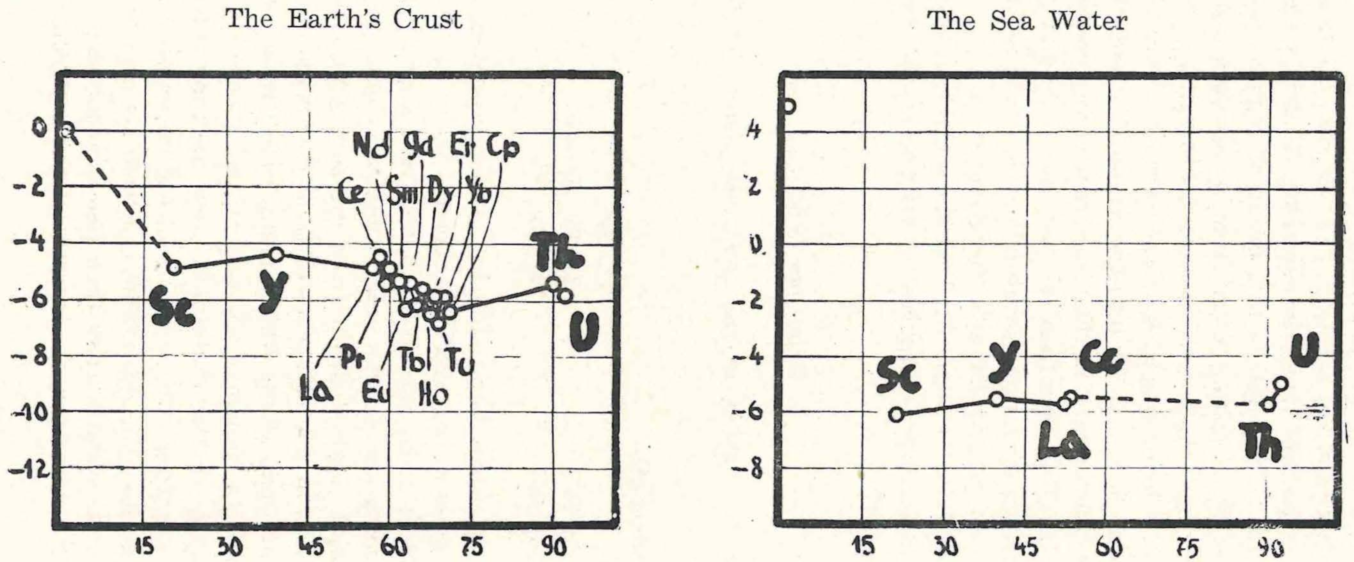
A connection with hydrogen *(H)* can not be established.

This group is the only one to confirm the Oddo-Harkins' rule claiming larger occurrence of elements denoted by even numbers as compared with those denoted by uneven numbers — but this applies only to the elements of this group occurring in the earth's crust.

It is to be expected from the foregoing that also other rare earths might occur in the sea water in quantities similar to the rare earths so far detected.

The group of actinides, as far as it results from available data, can only partially be added to the group IIIa, into which it is to-day usualy placed.

GROUP IIIa



The Earth's Crust

The Sea Water

Fig. 5

As evident from the preceding review of electronic outer orbits of this group, the actinides *(Th, Pa,* and *U)* differ a little as to their structure from the elements of the group II, but *Th* and *U* are fitting well in this group as regards their occurrence, whilst *Pa* is falling away from it, because, according to its place, *Pa* suits better to the curve belonging to the group Va, where it is being placed by some authors. *U* was earlier set into the group VIa, and *Th* into the group IVa, and this seems to be more appropriate if their occurences are considered. It would be, therefore, incorrect to set up a special group of actinides, basing upon their occurence in the earth's crust, owing to difficulty of placing *Pa* into the group III a.

We shall later on come back to the actinides, when dealing with the phenomenon of scarce occurrence of the elements of the seventh period.

Subgroup IVa

Here is the review of the electronic outer orbits of the group IV:

Head elements	*C*	2 /2.2
	Si	2,6 /2.2
Subgroup IVa	*Ti, Zr, Hf, Th*	2,6, 2/2
Subgroup IVb	*Ge, Sn, Pb*	2,6,10/2.2

Members of this subgroup have not yet been detected in the sea water unless we include *Th* (thorium) in it (Fig. 6).

As evident from the table above, the following should be noted regarding the earth's crust: the head elements belonging to this group *C,* and *Si,* differ from the subgroup both by their occurrence and by the structure of their electronic outer orbits.

There are indications which, along with further investigations, may bring a change of the ratio of occurrence between lead *(Pb)* belonging to this subgroup and hafnium *(Hf)* belonging to the subgroup IVb, in favour of the latter, with the result that the quantities (in gramatoms) of hafnium may overbalance lead *(Pb)* in the earth's crust. (See also the following paragraph dealing with comparison of elements of the subgroups »a« and »b«).

GROUP IVa

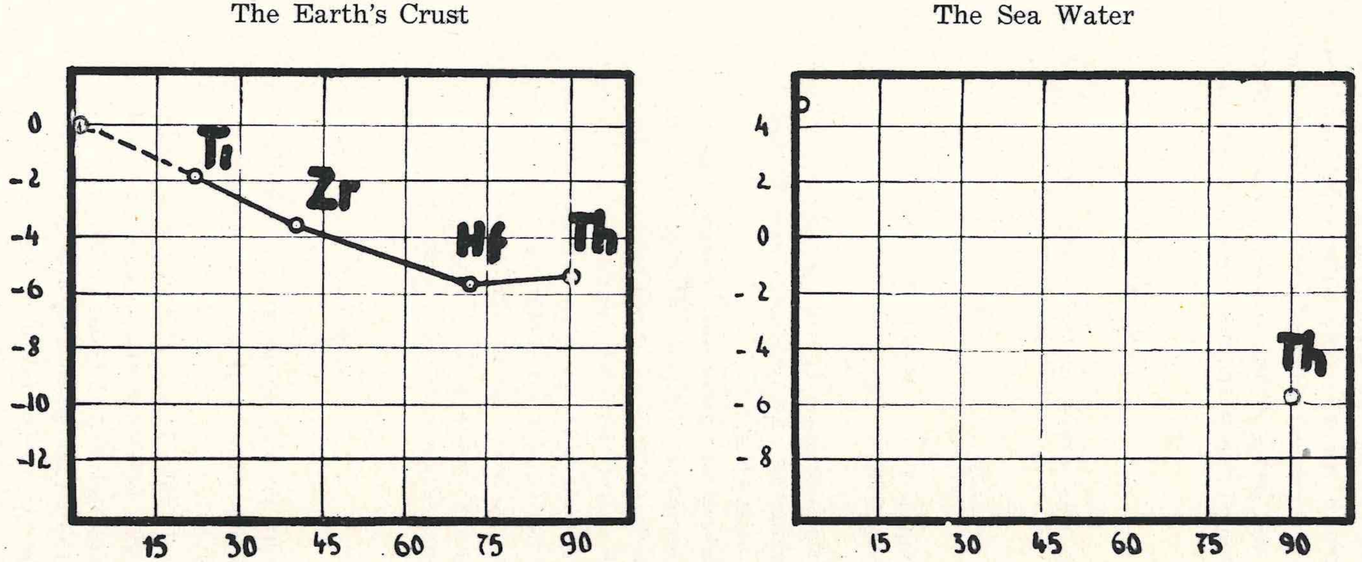


Fig. 6

Thorium fits well into this group, not only with regard to the structure of its electronic outer orbit, but also, as we see, regarding its occurrence as well (as has already been mentioned, thorium is still being grouped here by some authors).

(The connection with hydrogen *(H)* is easily established).

Subgroup Va

Here is the review of the electronic outer orbits of this group:

Head elements	*N*	2 /2,3
	P	2,2 /2,3
Subgroup V a	*V, Nb, Ta, Pa*	2,6,3 /2
Subgroup V b	*As, Sb, Bi*	2,6,10/2,3

Elements belonging to this group occur in the sea water in small quantities. According to recent data, only vanadium has been traced (Fig. 7).

More details are given on further pages on the occurrence of *V* (vanadium) in the sea water and on the inquire into the rule of predominance of elements belonging to the subgroup »a«. The possible quantity of *Nb* (niobium) occurring in the earth's crust is also dealt with on the subsequent pages.

Taking notice of their differences concerning the structure of the their electronic outer orbits, we separate this subgroup from the head elements, including the latter in the subgroup »b«.

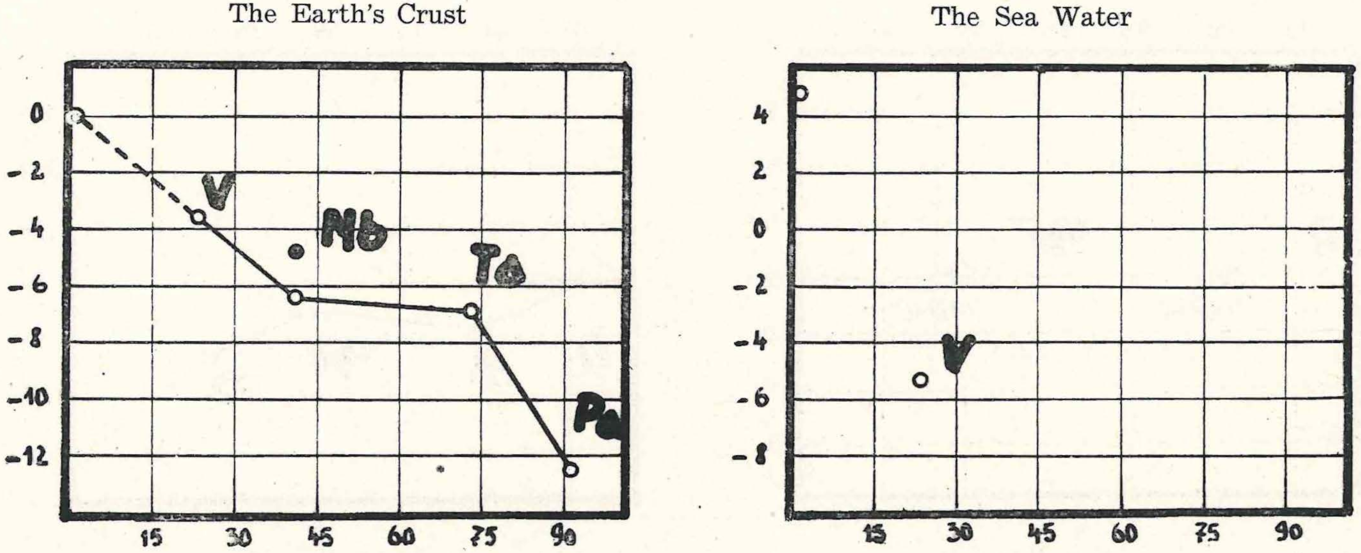
(The connection with hydrogen *(H)* is easily established).

Subgroup VIa

From our present knowledge it results that this group is contained in sea water only in part, as only *Mo* and *U* have been traced (Fig. 8).

It is likely that *Cr* might occur in sea water in larger quantities than *Mo*, and that the quantities of *W* (in gramatoms) may approximately equal those of *Mo* or *U*.

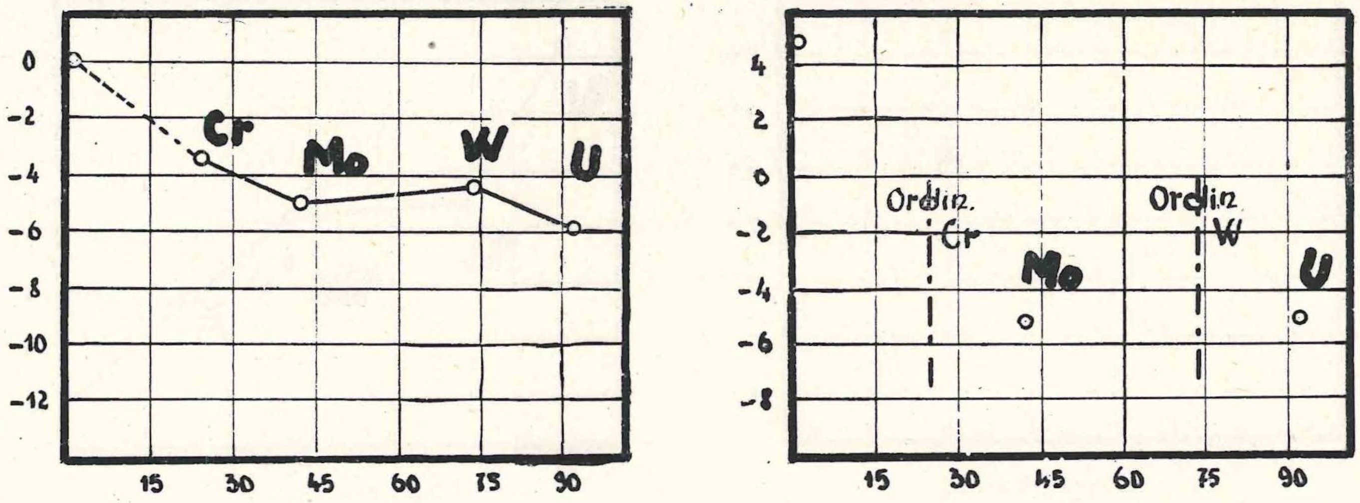
The anticipation concerning the quantity of *Cr* (chromium) is basing, on the one hand, upon the structure of curves, and, GROUP Va


The Earth's Crust

The Sea Water

Fig. 7

GROUP VIa

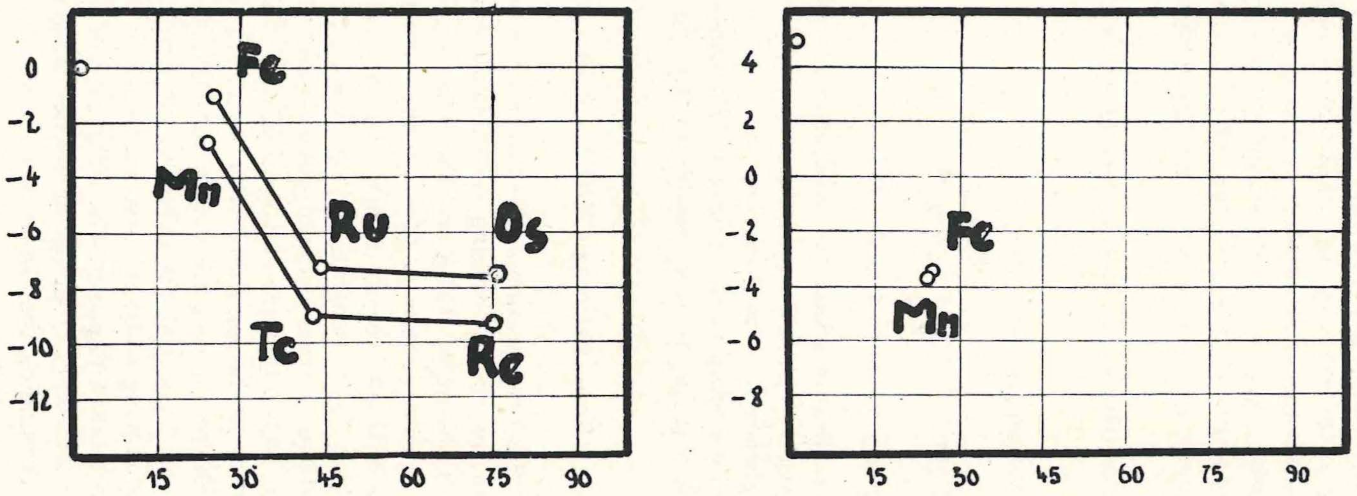


The Earth's Crust

The Sea Water

Fig. 8

GROUP VIII$_1$


The Earth's Crust

The Sea Water

Fig. 9

on the other hand, upon the rule of predominance of elements belonging to the subgroup »a« (see further pages), by considering the quantities of *Se* (selenium) that occur in the sea water. The probable quantity of *W* (tungsten) occurring in the sea water, judging from the structure of the curve for the group VIa, lies near the quantities of *Mo* (molybdenum) and of *Hg* (mercury).

Here is the review of the electronic outer orbits of this group:

Head elements	*O*	2 /2,4
	S	2,6 /2,4
Subgroup VI a	*Cr, Mo, W*	2,6,4/2
	U	2,6,5/1
Subgroup VI b	*Se, Te, Po*	2,6,10/2,4

This table shows that the head elements as to their structure, and regarding their occurrences as well, fall better in line with the elements of the subgroup »b«.

(The connection with hydrogen *(H)* concerning the curve of the subgroup »a« is only possible for the earth's crust).

Group VII a and VIII (= $VIII\text{-}_1$ & $_2$)

Only the first members of this group have been hitherto detected in sea water. Striking resemblance exists between the elements of the group VII a and the subgroup of iron, not only by the fact that subgroups *Mn* and the elements belonging to the group VIII are closely related by several chemical properties which these elements have in common in their bi- and trivalent form, or from common physical and chemical properties of e. g. elementary *Os* and *Re,* but also regarding their occurrence both in the sea water (Fig. 9) and in the earth's crust, as it results from curves showing a distictive parallelism between the group VIIa and the subgroup of iron belonging to the group VIII. Owing to their close relationship, the groups VII a and VIII are taken together. The subgroups of nickel and of cobalt differ somewhat from the mentioned subgroups *Mn* and *Fe* (Fig. 10). Arranging the elements after Mendeleeff, the natural

GROUP VIII$_2$

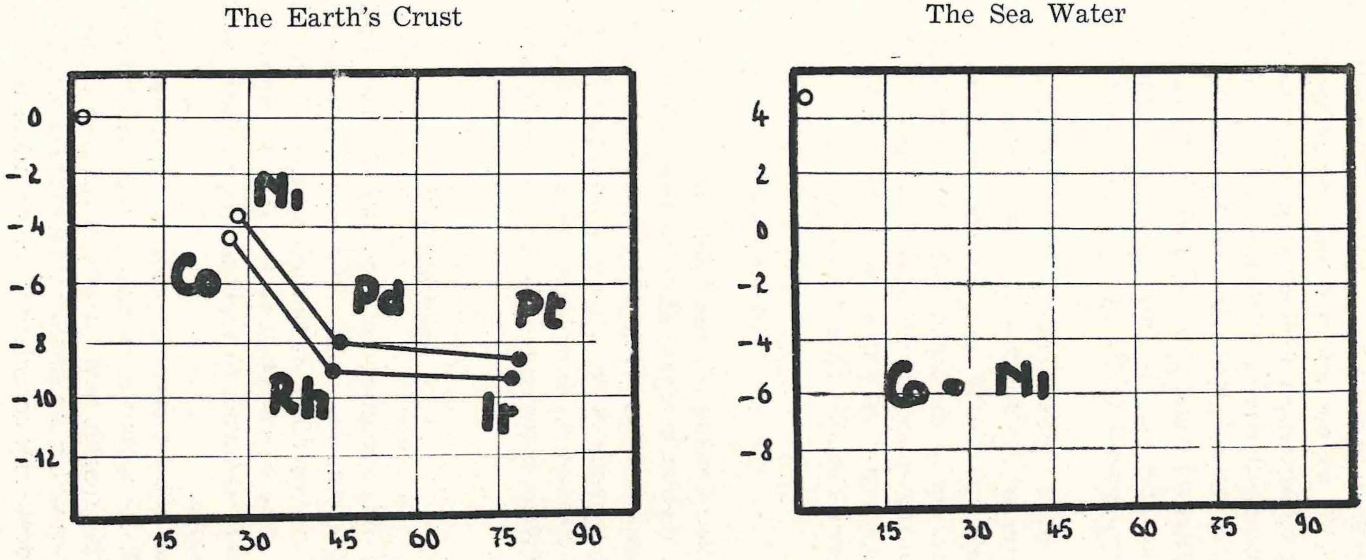


Fig. 10

continuity from group VIIa to group VIII would be split by the halogens (VII b), but this is avoided by arranging the elements according to Antropoff (Table 5), or according to Werner (Table 3). This similarity of structure of the curves illustrating the occurence of the subgroups *Mn, Fe, Ni,* and *Co,* is also to be met with subgroups I b and II b (see also Fig. 11 and 12). This statement is, in some way, another evidence proving the correctness of the rerrangement of the system of elements as given by Antropoff.

The earth's crust contains couples of elements related by the occurrence: *Fe-Mn, Ni-Co, Ru-Tc, Pd-Rh, Os-Re,* and *Pt-Ir.* Only *Fe-Mn* and *Ni-Co* may be traced in the sea water for the time being. As to the remaining four couples of elements belonging to the subgroup VII a and the group VIII, their quantities in sea water may likely be the same, but, of course, for some potencies smaller than *Fe* and *Ni.*

Subgroup I b

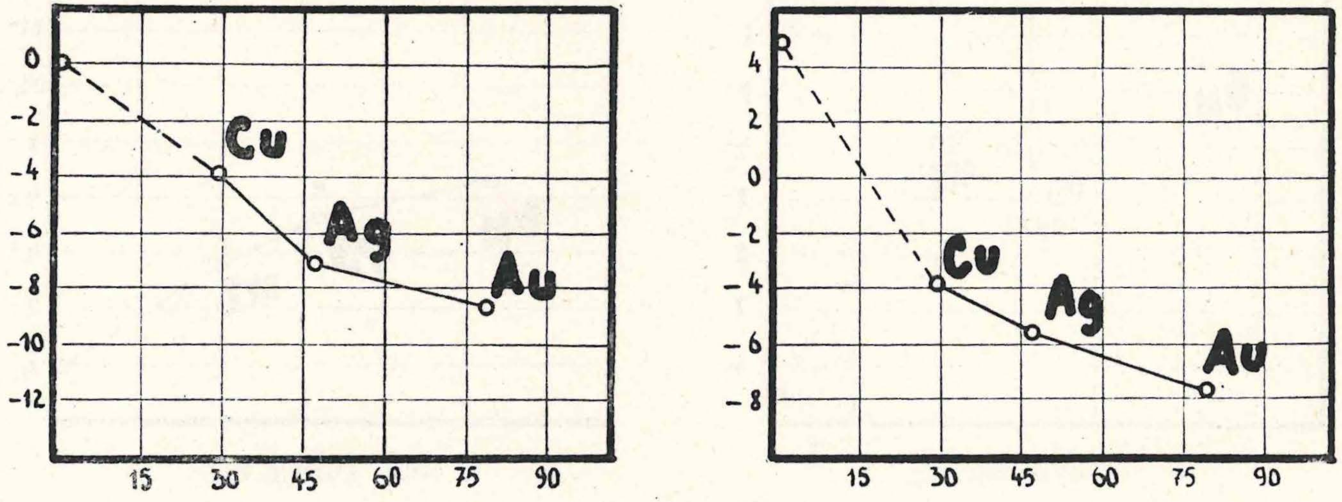
All the elements of this fubgroup occur in sea water and there is a regular decrease of occurrence following the increase of the atomic number, (Fig. 11). This fact, as well as the reciprocal relationship of the elements belonging to this subgroup, appear to concern the earth's crust also, thus showing a distinctive parallelism between the occurrence in the latter and in the sea water.

Subgroup II b

From this subgroup only *Zn and Hg* have thus far been discovered in the sea water. There is much resemblance between their occurrence in the sea water and the earth's crust (Fig. 12). The curves obey to the rule of relationship of the occurrence of elements to their atomic number, as in the majority of groups.

Cd has not yet been detected in sea water, but, as already mentioned, its presence in marine organisms has been determined. It is probable that quantities (in gramatoms) of *Cd* contained in sea water are smaller than those of *Zn.* This conclusion has been drawn by considering the parallelism of the curves.

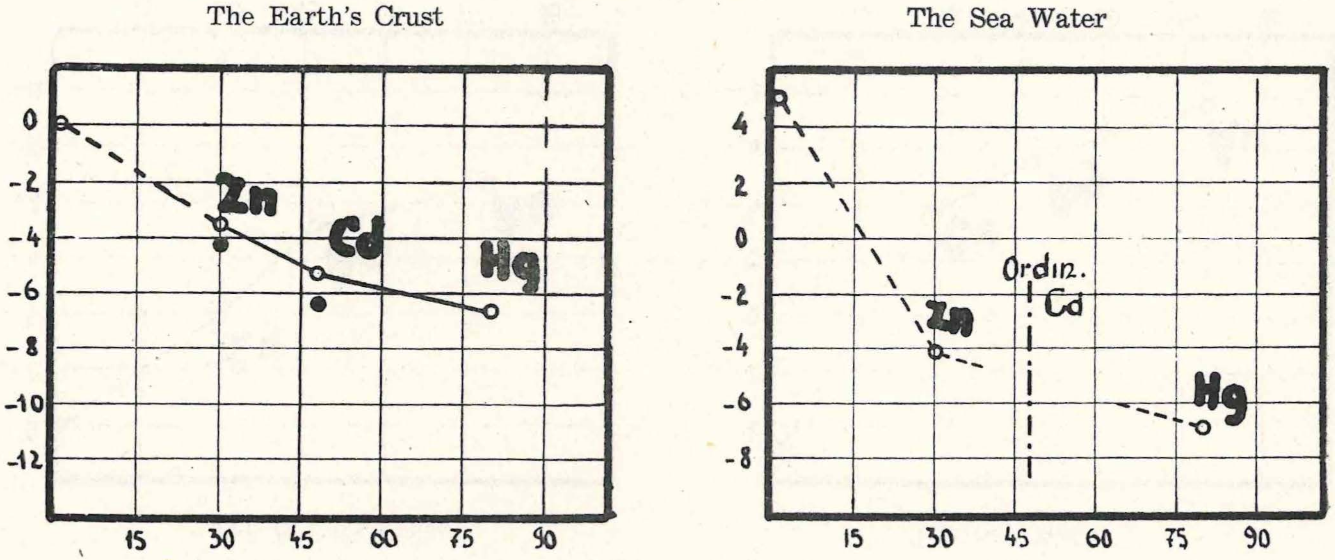
GROUP Ib


The Earth's Crust

The Sea Water

Fig. 11

GROUP IIb


The Earth's Crust

The Sea Water

Fig. 12

Subgroup III b

According to their properties, the head elements of group III join this subgroup. This fact is due not only to the structure of the electronic outer orbits (see the review of electronic outer orbits of elements belonging to subgroup III a), but also to the occurrence of elements of both subgroups (Fig. 13) in the earth's crust and particularly in the sea water, where the subgroup III b shows regular decrease of occurence corresponding to the increase of the atomic number.

There is a deviation from the regularity as far as the earth's crust is concerned, inasmuch as the first head element — boron — occurs in much smaller quantities than the second head element — aluminium. The decrease is otherwise diminishing with the increase of the atomic numbers, this gradually resulting in an almost horizontal line. It is probable that indium may occur in sea water in quantities not more than three potencies of a gramatom smaller in comparison with gallium. Judging from the curve of occurrence of elements in the earth's crust, it is likely that the quantity of thallium in sea water will show little difference in comparison with the quantity expected for indium.

Group IV b

All the elements of this group, with the exception of *Ge*, are known to be contained in sea water (Fig. 14).

The occurrence of elements is decreasing with the increase of the atomic number, but in a way that the rate of decrease is slowing down with the growth of the atomic number of elements. With regard to our rule concerning the functional relationship between the occurrence and the atomic number of an element within a group, we may expect that the quantity of germanium in 1 ton of sea water will amount about 10^{-3} gramatoms, i. e. it will be, in gross approximation, somewhere betwen the quantities of *Si* and *Sn*.

As already shown, the decrease of occurrence of elements belonging to this group is taking place without exception in sea water, while deviations appear in the earth's crust. So the first head-element — carbon — occurs in scant quantities.

GROUP IIIb

The Earth's Crust

The Sea Water

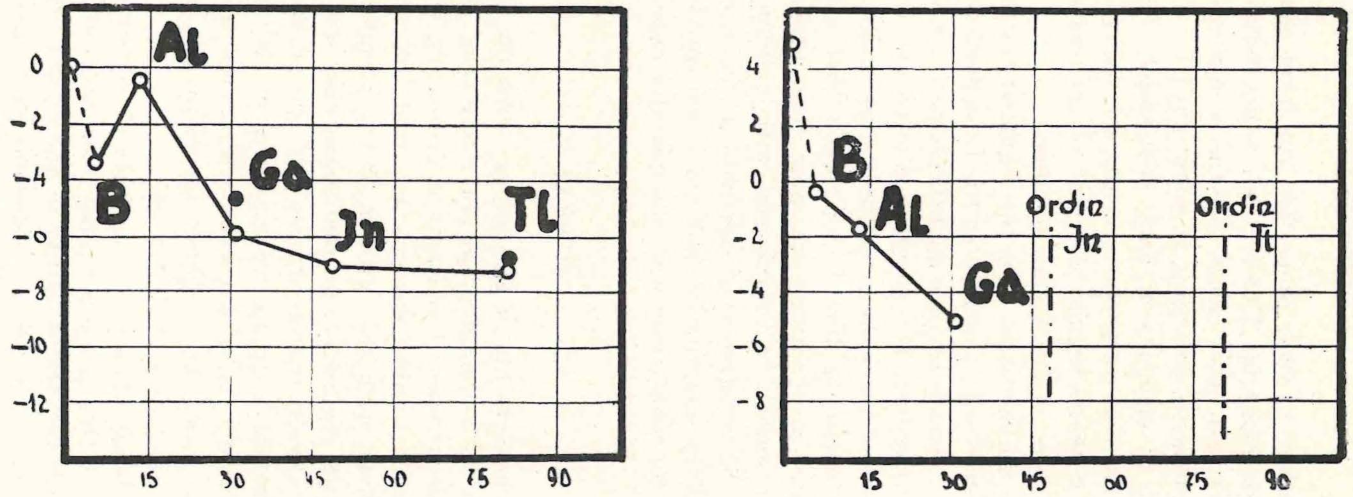


Fig. 13

Other deviations from this rule (germanium shortage) with regard to the same curve (for the earth's crust) are likely to be revised.

This is the more probable, since, according to some authors, the precentage of occurrence of germanium in the earth's crust has thus far not yet been established (Tućan, 1930). This is distinctly evident from the following. Estimating the quantity of distribution of germanium *(Ge)* in the earth's crust, Vernadski (V. Floroff — R. Judkevič, op. cit.) puts 0.0001%, whilst V. M. Goldschmidt (1933) had a higher estimate — 0.0004% — which has been increased by the same author (1937) to 0.0007%. (Fig. 14).

Estimating the quantity of distribution of tin *(Sn)* in the earth's crust, Vernadski puts 0.008%, whilst Goldschmidt (1937) gives 0.004%, i. e. the half of the foregoing. S. Miholić (1949) found similar quantities of occurrence of tin in Serbian carbonic granites. The values amount from 0.0056 to 0.0069% *Sn* in these granites, from 0.0028 to 0.0041% in Croatian green schists, and even from 0.001 to 0.004% Sn in Swedish granites. These values are in conformity with the estimates given by V. M. Goldschmidt (1937).

These estimates of occurrence of germanium in the earth's crust, and the estimates for tin, are likely to be revised in the course of further investigation, with the result in favour of germanium.

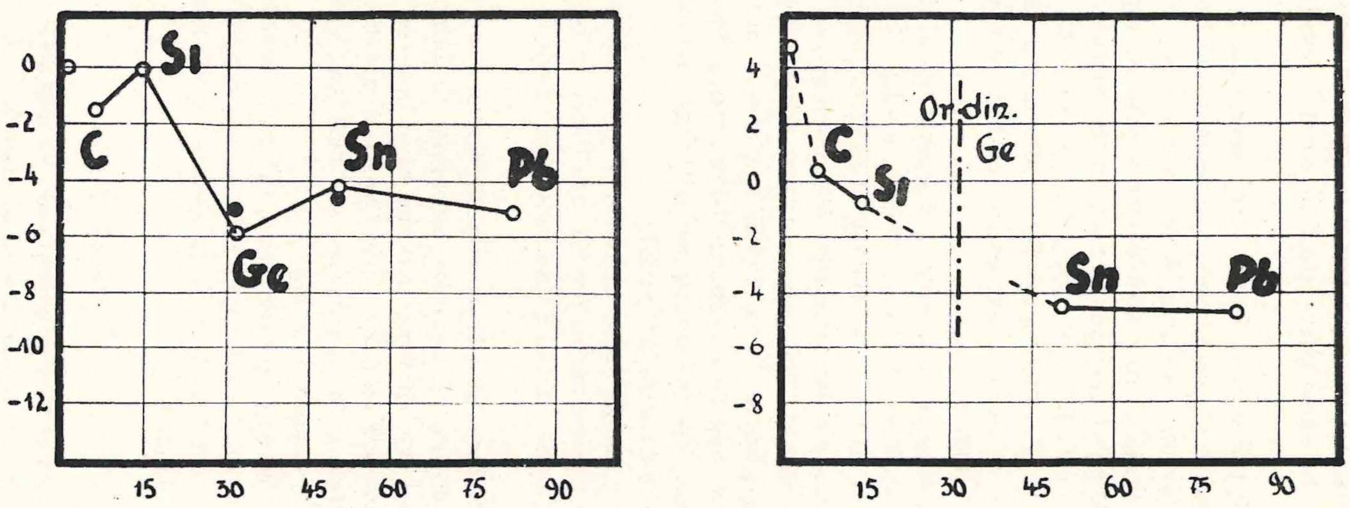
This follows also from considerations concerning the mutual relationship of elements belonging to subgroups »a« and »b« (see below), showing that the ratio between the quantities of the couple zircon *(Zr)* — tin *(Sn)* is suggesting that the difference between the occurrence of these two elements may be higher than supposed to-day.

It is also quite possible that the ratio between the quantities of lead *(Pb)* and hafnium *(Hf)* — see subgroup IV — occurring in the earth's crust, may undergo a change in favour of the latter element.

Group V b

Elements of this subgroup *(As, Sb* and *Bi),* as to their chemical properties, follow the head elements of the group. This

GROUP IVb



The Earth's Crust

The Sea Water

Fig. 14

is easily perceivable if we keep in view the structure of their electronic outer orbits. (See the structure of the electronic outer orbits of elements belonging to the group V). All the members of this group occur in sea water (with the exception of *Sb)*, their quantities decreasing with the increase of the atomic number. (Fig 15).

The graph suggests that quantities of *Sb* in sea water may amount from about 10^{-4} to 10^{-5} gramatoms per ton, or less than *P* and more than *Bi*.

It is supposed from some indications that the present estimate of quantity of *As* in sea water is rather high and that it may have resulted from partially including the similar *Sb* (see the paragraph dealing with the relationship of the subgroups »a« and »b«).

In the earth's crust the elements of this group also conform to rule of mutual relationship of occurrence to the atomic number and there is a regular decrease of occurrence following the increase of the atomic number. The only exception to this rule is the first member of this group — nitrogen — which is contained in the earth's crust for 1 1/2 potencies less than it should occur according to rule. (Such a deviation does not take place in the case of nitrogen in sea water). Here also the curve has the trend to become horizontal.

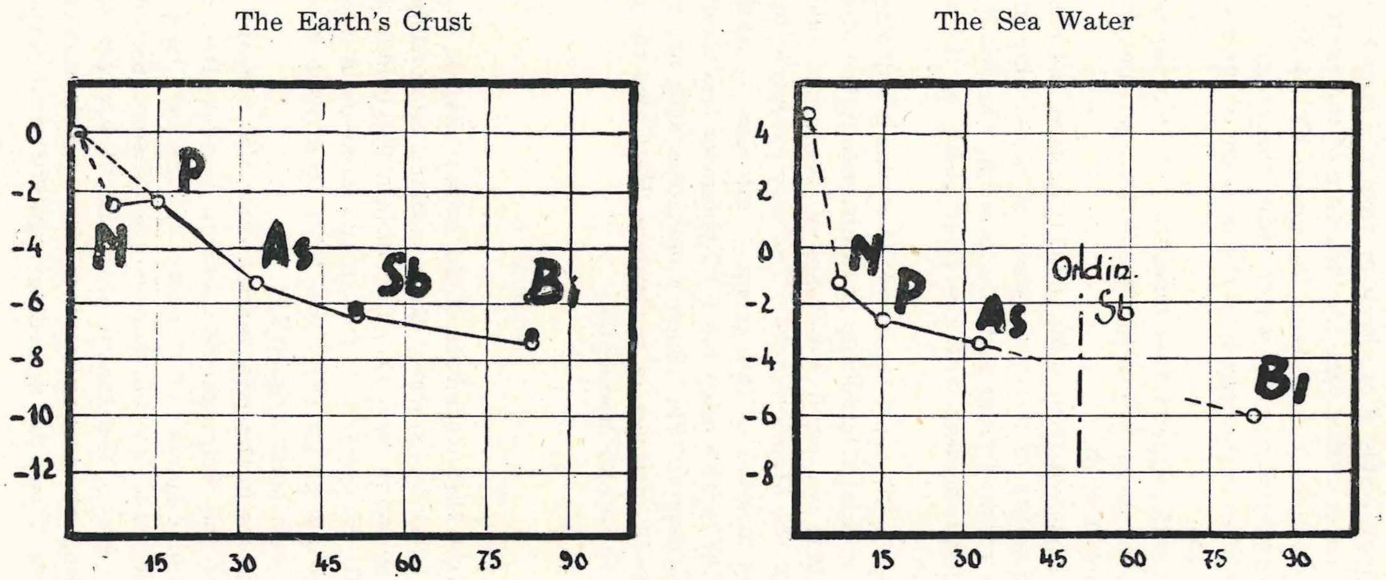
Group VI b

The first three members of the group, oxygen, sulphur and selenium, occur in sea water, the remaining two members, tellurium and polonium, have thus far not been detected in sea water. Along with the increase of the atomic numbers of elements belonging to this group (Fig. 16), their occurrence in sea water decreases with much regularity.

Conditions in the earth's crust show also full conformity to the rule of the reciprocal relationship between the occurrence and the atomic number of elements, but it should be pointed out that the decrease of occurrence is less conspicuous towards the end of the group, and that it altogether disappears with tellurium, passing even into an increase (rule of deflection of curves).

Judging from the preceding regularities of occurrence of

GROUP Vb



The Earth's Crust

The Sea Water

Fig. 15

GROUP VIb

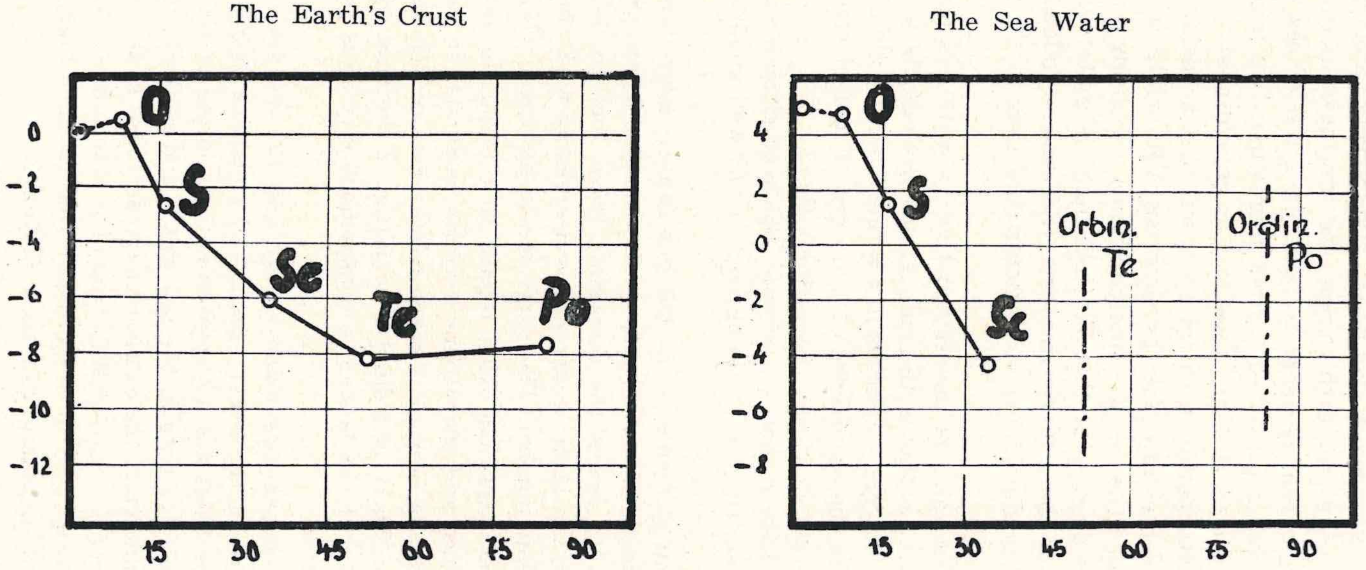


Fig. 16

elements as grouped in this paper, and from the analogous conditions found in the earth's crust, the conclusion may be inferred that tellurium is likely to occur in 1 ton of sea water in quantities that are smaller for not more than five potencies as compared with selenium (measured in gramatoms).

This anticipation of the minimal quantity is basing upon the structure of the curve for the subgroup VIb, whilst by considering the quantity of *Mo* (molybdenum) occurring in the sea water, we may suppose that *Te* (tellurium) is contained there in a quantity of about 10^{-7} gramatoms. (See also on following pages the rule of predominance of elements belonging to the subgroup »a«).

It should also be mentioned that — with regard to the earth's crust — this is the only group of elements whose first member — oxygen — occurs in a larger quantity than expected according to the occurrence of hydrogen. This fact concerns sea water also but it is less conspicuous there.

According to their occurrence, the head elements belonging to this group fit into the subgroup »a« as well an into the »b« one.

All four elements of the halogen family occur in sea water. The first member — fluorine — shows some downward deviations (Fig. 17), while the remaining three conform remarkably to the rule, viz. their occurrence is decreasing with the increase of the atomic number. The curve meets hydrogen *(H)*.

Similar conditions with regard to the mutual relationship of occurrence and the atomic number exist also in the earth's crust, differing only by a much slower rate of decrease of the occurrence. There is a similar deviation of the first member — fluorine — but not in such a conspicuous way as is the case in the sea water.

The observations made so far and the disclosed regularities concerning the other groups of elements would, perhaps, provide the basis for an approximate estimate of the quantity of astatine *(At)* both in the sea water and in the earth's crust. In this connection, the extraordinary decrease in the occurrence of radium *(Ra* — group II a) and of protactinium *(Pa* — group Va) should be kept in mind, a fact due to their high radioactivity and the unstability of their nuclei.

GROUP VII

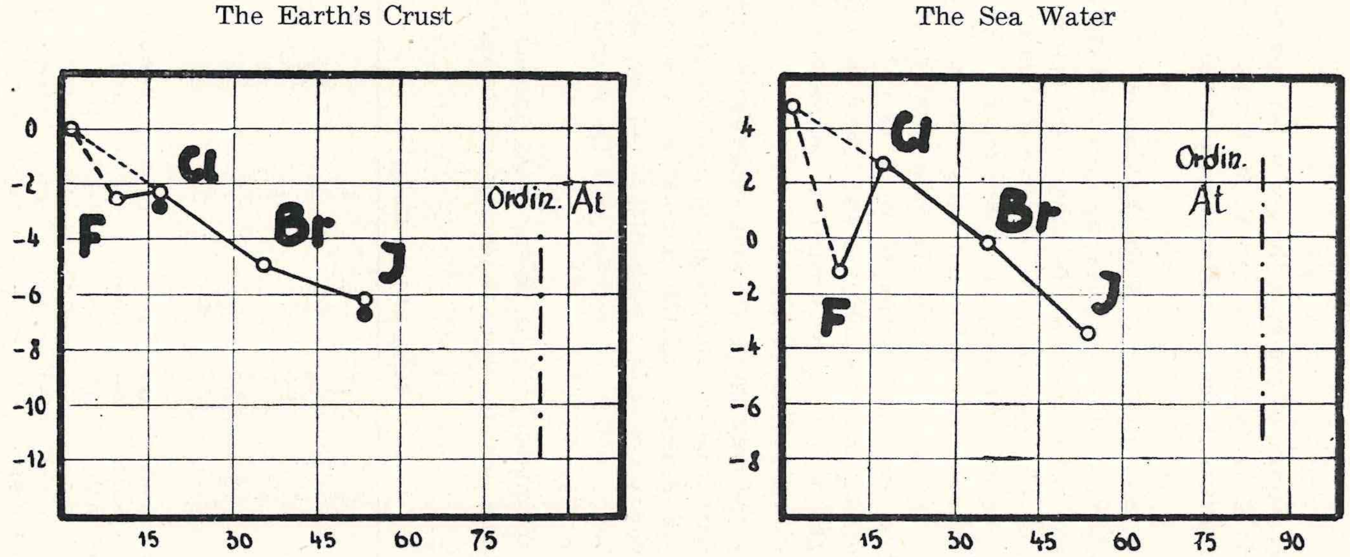


Fig. 17

Group O

The occurrence of argon in the sea water has been already determined. N. W. Rakestraw and V. M. Emmel (1938) found that its quantities in the sea water correspond to its saturation value.

W. D. Urry (1935) and N. W. Rakestraw, C. E. Herrick, and W. D. Urry (1939), investigating the conditions existing in the sea water with regard to the other inert gases, concluded, as in the case of argon, that the occurrence of these gases (helium — *He,* neon — *Ne,* krypton — *Kr,* xenon — *X)* in sea water is in good agreement with their occurrence in the atmosphere (Kalle, op. cit.). Utilizing the data concerning the occurrence of these gases in the atmosphere (L. Hock — 1934, page 450), concerning their solubility in water, and their density, we composed the data on their occurrence in the sea water (see Table 4, dealing with inert gases).

This is the only group showing considerable irregularities and deviations from our rule of group relationship between the occurrence of elements and the increase of the atomic number, this irregularity (shortage) taking place not only with the first head member — helium — but also with the second head member — neon (Fig. 18).

This fact might, perhaps, be due to the gaseous condition of these elements, which, owing to their inertness and inability to

Table 4

Table of Inert Gases

Symbol	Practical atomic weight	Solubility in water. Coefficient of distribution for 10° C — according to Oswald	Percentual occurrence in the atmosphere without H_2O and CO_2	Quantity of ml in 1 liter of water at 10° C	Weight per liter at 760 mm and 0° C	Occurrence in mg in 1 liter of water	Gramatoms per ton of sea water
He	4,002	0,0103	0,0005	0,00005	0,1783	0,00000918	$2,30 \times 10^{-6}$
Ne	20,183	0,0171	0,0018	0,00031	0,8985	0,0002785	$1,38 \times 10^{-5}$
Ar	39,944	0,037	0,932	0,345	1,7833	0,61	$1,5 \times 10^{-2}$
Kr	83,7	0,084	0,0001	0,000084	3,708	0,00031	$3,7 \times 10^{-6}$
X	131,3	0,180	0,00001	0,000018	5,851	0,000105	$8,0 \times 10^{-9}$
Rn	220	0,350	—	—	9,96	—	—

GROUP 0

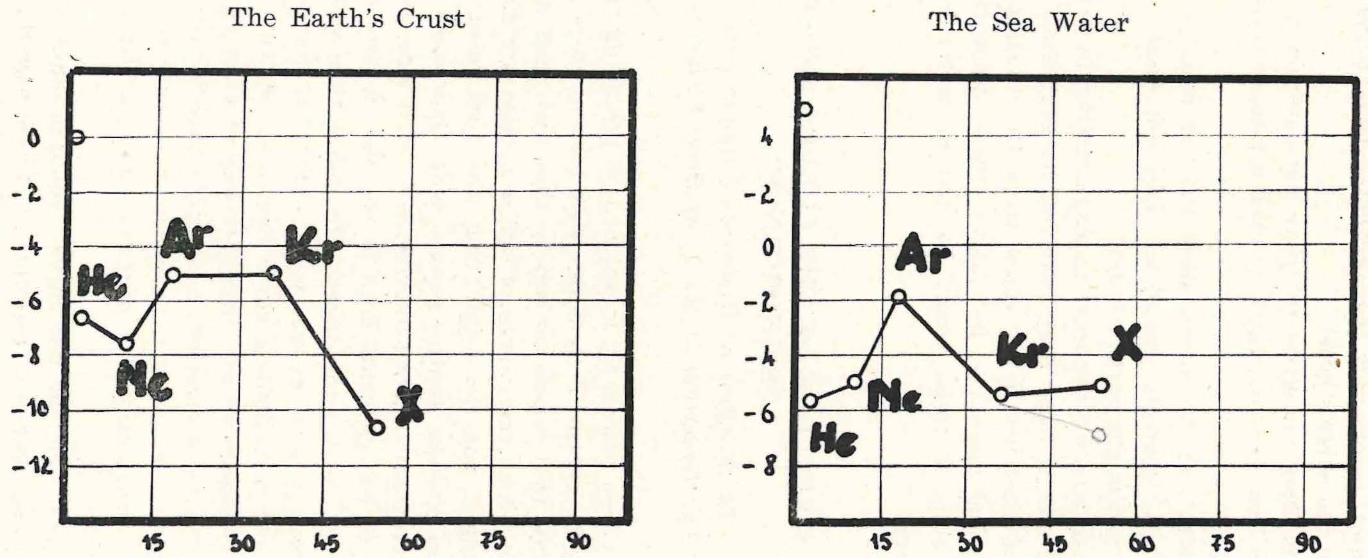


Fig. 18

form chemical compounds, are prevented from being fixed and retained in the earth's crust.

It is beyond our scope to treat the question as to when, where, and how, this shortage, or even a loss, of these light gases has taken place.

The data and the curves show that, as regards the occurrence of these elements, analogous conditions exist both in the sea water and in the earth's crust.

Revised data for the inert gases occurring in sea water, as given in Table 4, have been obteined by supposing their coefficient of solubility in sea water to be the same as for distilled water, and moreover, by taking their quantities in the atmosphere as if there would be neither water vapour nor carbonic acid.

THE STRUCTURE OF THE CURVES AND THEIR SIGNIFICANCE

The Position of Hydrogen in the Curves

The Deviation of the First Head Elements

It has been repeatedly mentioned on preceding pages, when reviewing the groups of elements, that the curves of groups follow a course that makes us believe that hydrogen was the element from which the curves of single groups are starting, viz. that hydrogen was the originating, the first head element of each of the groups, (entire groups with their head elements). This observation concerns likewise the conditions pertaining to ocurrence of the elements both in the sea water and in the earth's crust. As already shown, the connection with hydrogen is not always possible by merely extending the line in a straight direction, but sometimes a curve has to be drawn.

It is necessary to say that this way of treating the curves of single groups of elements is suitable only for our method of exposition, viz. by using the system of coordinates having the arithmetic progression for abscissae and the logarithmic one for ordinatae.

It is likely that all our curves would develop into hyperboles in a normal system of coordinates. These hyperboles are supposed to be of a very deep kind, tending to degenerate into right angles. In such a case the connection between hydrogen *(H)* and single group curves would never be a straight line.

Figures 19 and 20 should be taken for examples. Their right sides have been drawn in the way to let the values of both coordinates run linearly, thus producing a true picture of actual conditions.

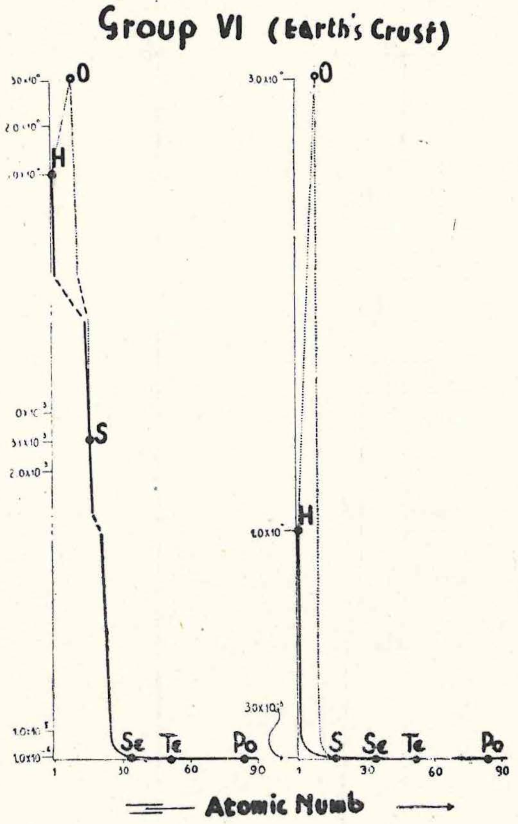


Fig. 19

The curve, connecting the elements of this group, is evidently a hyperbole running through the point of hydrogen. The shortcoming of this way of illustration consists in not bringing to view the differences existing between single elements with higher atomic numbers, owing to the vast overbalance of the first elements of the group.

(If we would like to have these differences markedly shown

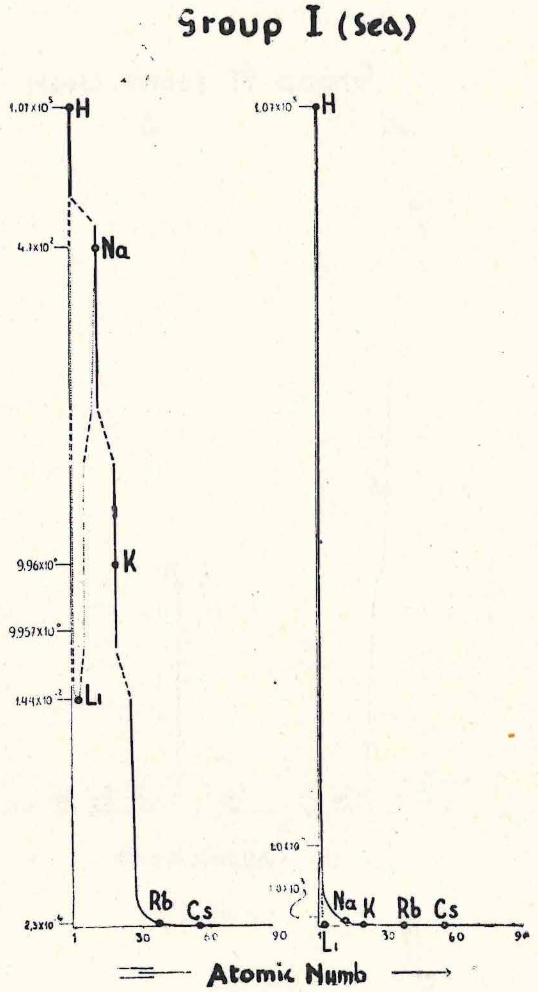


Fig. 20

by this linear system of coordinates, diagrams on paper hundreds of meters long should be made!)

The left sides of the pictures have been drawn by composing the ordinate from several differently measured parts. This is actually a middle way between a simple linear scale as applied on the right sides of the pictures and the logarithmical scale as on figures 3—18.

In the system as applied on the right sides of the figures 19 and 20 hydrogen is again the point through which hyperboles of all the groups of elements are likely to run. What is the significance of these hyperbolical curves? Does this mean that we have here a natural phenomenon, developing itself from changes of two variables, which, tightly pressed into a rigid and simple rule, display the characteristic feature of all the processes able to be shown by the hyperbole, e. g. the Boyle-Mariotte Law? There volume and pressure (at a stable temperature) vary in inverse relation, and here again are inversely related the total quantity of elements and their atomic mass (the atomic number, Z).

It has actually been pointed out in the literature that this decrease of occurrence of elements may have some connection with the stableness of nuclei of their atoms. Goldschmidt (1934, page 902) has it that the decrease of occurrence of elements is associated either with the phenomena of stableness of atoms or with those of their disintegration. Atoms with larger nuclei are the less stable ones. It is quite clear to-day that there is some relationship between the occurrence of elements and their disintegration and that the actually present quantity of a kind of atomic nucleus is taken as the measure for the probability of its existence.

Let us handle now our curves (Fig. 3—18) in the frame of reviews given in this paper.

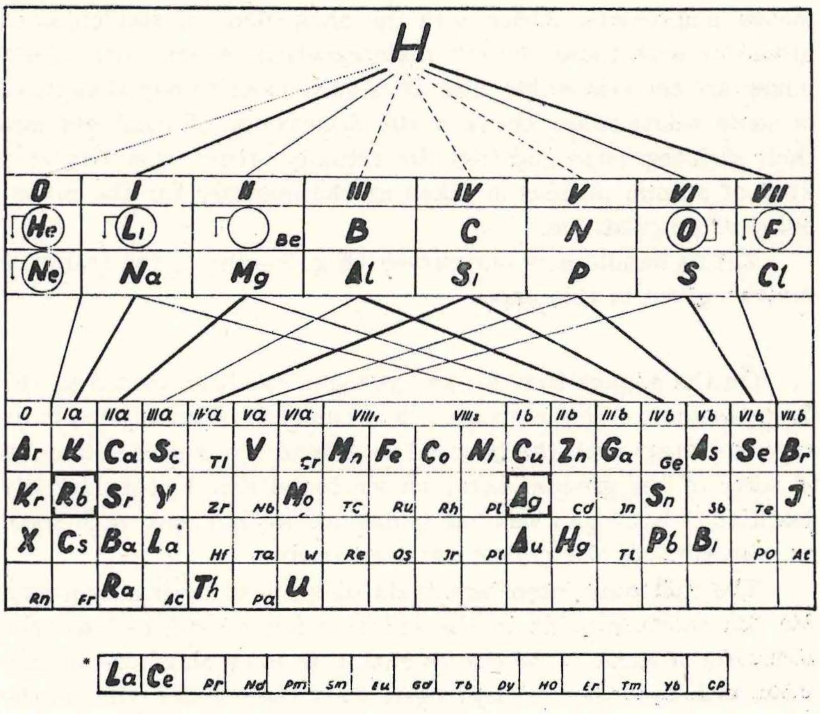
On the graphs Nos. 3—18 hydrogen has been placed as the first member of single groups. This has been originally made as an experiment with the purpose to extend the curves belonging to some of the groups. Later on we found it to be considerably justified if hydrogen was left connected in that way with some or even with all the groups simultaneously.

The following important facts underlie to taking hydrogen for the starting point in the construction of curves: a) the structure of some of the curves enable us to establish the connection with hydrogen; b) hydrogen bears the number one on the list of elements; c) hydrogen, according to its occurrence in the earth's crust, is second only to oxygen.

(As to the occurrence of oxygen we should remark the following: did not, perhaps, such a quantity of this element — unlike hydrogen -- grow in a secodary way, as a stable product resulting from nuclear reactions, in analogy with the accumulation of helium in some places outside the Earth at the expense of the light elements — *Li, Be, B,* etc?).

The group of the alkaline metals, alkaline earth metals, and of halogens (excluding from all of them the first head elements, lithium, beryllium, and fluorine), obviously illustrate the relationship betwen the curves of groups and hydrogen. This is why — on Tables 5 and 6 — the lines of junction of these groups with hydrogen have been markedly drawn, and why *Li, Be,* and *F,* are followed by a sign to indicate their impairing occurrence. It is interesting, indeed, how even in this way the pecu-

Table 5



liar position of hydrogen among other elements becomes noticeable. Hydrogen is well suitable to head the first group of alkaline metals, where it is usually being placed in the periodic system with regard to some kindred momenta, e. g. HCl comparable to $NaCl$, KCl, and the like.

Hydrogen can also well be placed as the first element of the group VII of halogens, thus taking the place allotted to it by K. Moers in the year 1920, owing to the behaviour of LiH at electrolysis, where *H* is being separated on the anode, like *Cl.*

But hydrogen is suitable to head other groups also, with the difference that the lines of occurrence of elements of single groups cannot be connected by a straight line but by a curve.

Trying to illustrate the degree of association of single groups with hydrogen, various junctions of hydrogen *(H)* with the head elements from Tables 5 and 6 are given. (Prout's hypothesis!).

It should again be noted that the first head members of groups often deviate from the rule, this concerning all the elements of the second period in the earth's crust and the majority of them in the sea water. Deviations pertaining to the elements of the second period are marked by an arrow on the Tables 5 and 6.

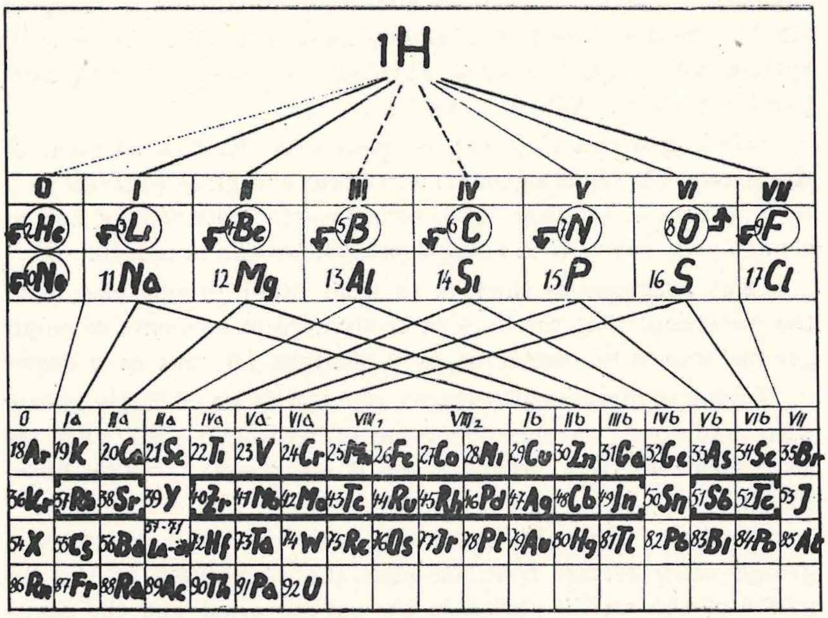
It is interesting that this deviation of *Li, Be, B,* and some other head elements of the first period, does not occur only in the earth's crust and in the sea water, but, according to Goldschmidt (1934) also in the atmosphere of the sun.

H. Bethe, J. Gamoff, and E. Teller, produced theories to explain the shortage of light elements in the sun and other stars, where they represent the matter from which the stars are getting their energy (L. Čermelj, 1948; A. G. Masevič, 1949).

(According to our method, the relationship between hydrogen and the groups O and VIII is less evident).

Basing upon the foregoing observations we put hydrogen on the Tables 5 and 6 above all the groups, as their starting point, in conformity with the arrangement of the periodic system of elements as given by A. Antropoff, where the groups O and VIII have also been separated from *H.*

Table 6



As already known, the head elements of the single groups of the periodic system of elements (2nd and 3rd period) bifurcate into two subgroups, »a« and »b«, with the exception of the groups O and VIII.

The head elements of the lower groups (particularly I and II) are nearer to their subgroups »a« by many chemical properties, while the trend of the head elements to come closer to the subgroups »b« is the more manifest the further we proceed towards the higher groups.

As it results from our data concerning the occurrence of elements they behave similarly with regard to their properties. The head elements of the first group are followed by their subgroup »a«, this being particularly well evident in the sea water. This is the reason why, on the Table 5, the connection of Na with the subgroup I a is marked by a conspicuous line and the connection with the subgroup Ib by a thin line.

In the sea water, the head elements of the group II are also followed by the subgroup »a«, and *Mg* on Table 5 is connected by a thick line with *Ca* from the subgroup II a, while it is connected by a thin line with the subgroup II b, because there is neither a link nor continuity between the occurrence of *Mg* and of the elements of the subgroup II b.

The head elements of the group III, clearly characterized by their acidity, are associated with their subgroup »b«, having in common also their chemical characteristics, and, in sea water, the quantity of occurrence. Aluminium is followed by gallium from the subgroup III b and not by the elements of the subgroup III a, thus agreeing with the condition in the earth's crust. This is shown on Tables 5 and 6 by corresponding thick and thin connecting lines.

This enables us keep in view, through all the groups, how the head elements are followed by their subgroups »b« (thick lines!) up to the group VII.

It is almost an exclusive rule with sea water that the head elements are followed by only one subgroup in the aforesaid way.

There are, on the contrary, many cases concerning the occurrence of elements in the earth's crust, where the line of the head elements, bifurcating, proceeds likewise gently towards both subgroups, »a« and »b«. Such a picture offer the groups I, II, IV, V, and VI as far as the earth's crust is concerned. (See Table 6).

GENERAL CHARACTERISTICS OF THE GROUP CURVES

The Rule of Deflection

The Rule of Decrease

As mentioned on the preceding pages, the relationship between the occurrence of the elements and the increase of their atomic number is characteristic for each group separately, and each group should therefore be observed separately.

Deviations of the first head members have been given for all the groups with regard to the earth's crust and for some of them with regard to sea water.

As already seen, the majority of complete groups, and the remaining subgroups (according to Werner's method these are all groups — see Table 3), conform to the rule of relationship between the occurrence and the atomic number. But the degree of their dependance is rarely uniform, (as e. g. in sea water: *B-Al-Ga,* or *Na-K-Rb,* or *Cl-Br-J)* and the rate of decrease grows smaller from element to element.

A considerable number of curves of occurrence for the groups of elements show a regular deflection of the line when the corresponding element from the fifth period is reached causing the decrease to cease. This is the rule of deflection of curves at their elements from the fifth period, or, shorter, the rule of deflection of curves.

There are cases when this deflection is of such an extent that an increase of occurrence follows the increase of the atomic number: the line bends upwards. Such is the case with the earth's crust as regards the subgroups IIIb, VIa and b, and VIII — *Ni.*

On Table 6 the elements of the fifth period whose curves are subject to aforesaid deflection are marked by a frame. It results therefrom that this rule is applicable to all the elements of the fifth period, with the exception of the group of inert gases; the group IIIa which has a peculiar behaviour also in some other respects; Sn — the subgroup IVb — (which has been dealt with as regards its relationship with germanium); and iodine *(J)* — the subgroup VIIb — owing to the the fact that the occurrence of the member of the sixth period is still unknown.

Taking as a basis this rule of deflection, a conclusion may be drawn that, for instance, the quantity of niobium *(Nb)* occurring in the earth's crust as given by Goldschmidt (0.0015% ; — 1937) is overestimated, because the curve of the group Va, if drawn according to this estimate, would infringe the rule, which does not happen with data taken from Russian authors (0.000032%). (Fig. 7).

But some indications suggest, on the other hand, that the latter value is rather underestimated (see below).

In the majority of cases our knowledge of the occurrence of the elements in sea water is not complete and often only one member of a subgroup is known (elements still undetected in the sea water are printed in small letters on Table 5). So it is impossible to ascertain how far conditions in the sea water agree with those of the earth's crust. We can so far state for the sea water that the mentioned deflection of curves takes place when the elements of the fifth period in the subgroups Ia and Ib are reached, while Sr, judging from available data, does not conform to rule. It would, however, be advantageous to revise once more the ratio between the quantities of strontium *(Sr)* and barium *(Ba)* occurring in the sea water.

According to the unconfirmed data given by the Russian Biochemical Laboratory in 1937 (A. P. Vinogradoff, 1938), the quantity of strontium *(Sr)* occurring in the sea water would amount to 8.0 g/t. This quantity of *Sr*, being in better agreement with the rule of deflection of the curves, almost eliminates the exception from the rule.

There are data suggesting another regularity, similar to the rule of deflection given above. This concerns the behaviour of the elements of the seventh period consisting in an extraordinary shortage of occurrence of all these elements, whereby the curve of the respective group is being again bent downwards. Let us call this the rule of decrease of elements of the seventh period of the system of elements.

This is clearly visible with the groups II a *(Ra)* and Va *(Pa)*, and it may be expected also from other elements bearing the atomic numbers 87—92, which are likely to be followed by the transuranic elements, too.

The explanation thereof should, in all probability, be sought in the fact that the nuclei of these elements are extremely large and complex, being, moreover, very radioactive, thus unstable. Thorium, and, to some extent, also uranium, whose half periods of disintegration are very long, make, however, exceptions from the above rule.

If, however, the elements with atomic numbers from 89 onward were put among the actinides, analogously with rare earths, the application of the Oddo-Harkins rule world here again be possible, as in the case of rare earths. This is due to the fact that both thorium and uranium possess even atomic numbers and occur in larger quantities than their uneven neighbours. It is possible that this observation will concern the transuranic elements as well.

As regards the group III a, it has already been pointed out that both for the sea water and for the earth's crust, its curve show an almost horizontal run.

The curve belonging to the group IV b shows an irregular run, caused by the place taken by germanium. Judging from many indications, the estimate of occurrence of this element in the earth's crust is likely to be revised, viz. increased in the course of further investigations.

No particular comment is needed for the curves of the remaining groups.

THE MUTUAL RELATIONSHIP OF OCCURRENCES OF THE ELEMENTS PERTAINING TO SUBGROUPS »A« AND »B«

The Rule of Predominance of Elements Belonging to Subgroups »a« of the Periodic System of Elements

To facilitate the observation of this relationship data are given on Table 7 for sea water and on Table 8 for the earth's crust. It is evident from these tables that there is some regularity which can be formulated as follows: elements belonging to subgroups »a« occur in larger quantities than their correlative partners from subgroups »b« (provided that the compared elements are of the same period). Let this regularity be called »Rule of the predominance of elemnets belonging te subgroups »a«. This rule is clearly shown by the conditions found in the earth's crust, while data relative to sea water are still insufficient. Beside examples within some groups of elements in sea water, which do confirm this rule, a few exceptions have also been found.

Let us now try to explain these exeptions.

Both in the sea water and in the earth's crust [(taking for the latter the data concerning the occurrence of gallium according to Goldschmidt (1937)] we find the ratio between *Sc* and *Ga* to be favourable to the group »b«. The question arises whether this circumstance belongs to characteristics of the group III which also otherwise shows some differences if compared to other groups of the system of elements, or has the estimate of the quantity of occurrence of these elements been provisionally unfavourable to scandium (*Sc*)?

A further exception from the above rule of predominance of the subgroups »a« is shown by the case of lead (*Pb*) and of hafnium (*Hf*) in the earth's crust, where the partner »b« (*Pb*) is outbalancing its partner »a« (*Hf*) for about 3.5 times.

The explanation of this case may be contained in the fact

Table 7

The Mutual Relationship of the Elements Beloging to Subgroups »a« and »b« in the Earth's Crust

Member „a“	Member „b“	Member „a“ Predominating for	Member „b“ Predominating for
K	Cu	3.8×10^2	
Rb	Ag	3.8×10^2	
Cs	Au	2.9×10^3	
Ca	Zn	2.65×10^2	
Sr	Cd	9.1×10^1 (1.0×10^2)	
Ba	Hg	1.4×10^3	
Sc	Ga	9.1×10^0	(1.7×10^0)
Y	In	6.4×10^2	
Ti	Ge	9.1×10^3 (1.3×10^3)	
Zr	Sn	4.0×10^0	
Hf	Pb	—	3.5×10^0
V	As	6.0×10^1	
Nb	Sb	(2.0×10^1)	1.4×10^0
Ta	Bi	2.7×10^0 (1.3×10^0)	
Cr	Se	5.4×10^2	
Mo	Te	$1,3 \times 10^3$	
W	Po	1.5×10^3	
Mn	Br	1.5×10^2	
Tc (Ma)	J	—	7.8×10^2
Fe	Mn	4.0×10^1	
Ru	Tc (Ma)	5.0×10^1	
Os	Re	5.0×10^1	
Ni	Co	1.0×10^1 (1.2×10^0)	
Pd	Rh	4.7×10^0 (1.0×10^1)	
Pt	Ir	2.0×10^1 (5.0×10^0)	

Remark. *The values in brackets have been obtained from* ***V. M. Goldschmidt's*** *data* ***(1937)****, and the remaining ones from Russian authors (all according to Table 2).*

Table 8

The Mutual Relationship of the Elements Belonging to Subgroups »a« end »b« in the Sea Water

Member „a"	Member „b"	Member „a" Predominating for	Member „b" Predominating for
K	Cu	6.3×10^4	
Rb	Ag	7.8×10^1	
Cs	Au	1.0×10^3	
Ca	Zn	1.3×10^5	
Ba	Hg	2.6×10^3	
Sc	Ga	—	$8\ 0 \times 10^0$
V	As	—	$5\ 0 \times 10^1$
Mn	Br	—	4.4×10^3
Fe	Mn	2.0×10^0	
Ni	Co	Equal	

that hafnium *(Hf)* has been recently discovered (1922) and that its occurrence is not sufficiently and exactly determined. Further investigations may probably prove that the occurrence of hafnium is larger than that of lead.

When this paper was already written and ready for print Prof. Dr. S. Miholić (Zagreb) has been kind enough to put at our disposal the results of his researches concerning the quantities of lead *(Pb)* occurring in some crystalline rocks.

This author found the following average quantities of lead *(Pb)*:

in a granite gneiss from Sweden (Forshem) . . $4.09 \times 10^{-4}\%$

in a green schist from Croatia (Medvednica) . . $2.02 \times 10^{-4}\%$

the average quantity of *Pb* in crystalline rocks being $3.05 \times 10^{-4}\%$ — The determinations were made polarographically (S. Miholić. Unpublished).

Whilst according to formerly available data the quantity of lead *(Pb)* occurring in the earth's crust amounted to $1.6 \times 10^{-3}\%$, it follows from the above data given by S. Miholić that the occurrence of this element in the earth's crust is actually much smaller.

This may be taken as a new evidence proving the tendency which conforms to our rule of predominance of elements belonging to subgroups »a«; in this way the exception observed with the the couple *Hf* — *Pb* (the latter element outbalancing its partner for 3.5 times) is caused to disappear, as according to Miholić the quantity of lead *(Pb)* appears to be much smaller, thus reversing the ratio between these two elements in favour of the partner »a« *(Hf)*.

As regards the couple *Nb* — *Sb* (see Table 7), there is no inconsistence with our rule of predominance if data are taken according to Goldschmidt (1937), but the case is reverse when data from Russian authors are applied. But, on the other hand, the Goldschmidt data for *Nb* are so high that they are inconsistent with the rule of deflection of the curve (see page 56), this suggesting that the actual quantity of *Nb* lies somewhere between the two quoted estimates.

The elements of the *Mn* and *Fe* series occur in approximately similar quantities, but the quantities of the partners of the *Fe* series *(Fe, Ru, Os)* predominate for about ½ potency. Also the elements of the *Co* and *Ni* series occur in similar quantites, the elements of the *Ni* series *(Ni, Pd, Pt)* being outbalanced for less than ½ potency.

This, however insignificant, predominance of occurrence of heavier elements over the lighter ones — this inversion — is interesting inasmuch as it concerns the group VIII of the system, which is otherwise known to occupy a particular place in the table of the system of elements. We should also mention that just here we meet another »anomaly« which was a considerable obstacle for the arrangement of the table of the periodic system of elements. Such is the case with *Co* and *Ni*, where *Co*, in spite of its higher atomic weight, has been placed in the table of elements before the lighter *Ni*.

The mentioned predominance of the *Fe* and *Ni* series over the *Mn* and *Co* series is an argument that apparently disagrees with our rule of the predominance of elements belonging to subgroups »a«. This argument, however, looses its validity if the elements belonging to subgroups »a« resp. those belonging to subgroups »b« are grouped as represented in the table 9.

This inversion, namely, when series of heavier elements take the part of subgroups »a«, is partially consistent with the above mentioned behaviour of *Co* and *Ni*. In the Table 5, 6, 7 and 8 the elements of the groups VIIa and VIII have been treated according to this criterion.

In the case of the couple manganese *(Mn)* and bromine *(Br)* the partner »b« *(Br)* appears to be in the sea water for about four potencies more frequent than its partner »a« *(Mn)*; and, in the earth's crust, the partner »b« *(I)* of the couple masurium *(Ma)* and iodine *(I)* does again overbalance for several potencies (see Tables 7 &8). This may be explained by the fact already pointed out when reviewing the single groups, viz. that the subgroup VII a [including manganese *(Mn)* and masurium *(Ma = Tc)*] tends, as already stated when reviewing the groups, toward the group VIII as regards their occurrence both in the sea water and in earth's crust, so that the subgroup VIIa could easily be considered a part of the group VIII, owing to their striking resemblance and similar distribution. Their chemical properties also bear likeness, resulting from their neighbouring place in the periodic system of elements (see Table 3). By taking the subject in this way, there would be no subgroup within the halogens, and comparison between bromine and manganese, and of the other above mentionel couple, would not be necessary.

Table 9

VIII/1		VIII/2	
b	a	b	a
Mn	Fe	Co	Ni
Ma (Tc)	Ru	Rh	Pd
Re	Os	Ir	Pt

The following groups from the Table 3 would be comparable among themselves:

1	to	11	4	to	14
2	»	12	5	»	15
3	»	13	6	»	16

The groups 7 to 10 would become independent central groups, splitting into two more akin couples, 7 (*Mn* series) and 8 (*Fe* series); 9 (*Co* series) and 10 (*Ni* series).

We come now to the halogens (18) and to the inert gases (O), which, perhaps, would be comparable among themselves, the halogens playing, with regard to occurrence, the part of the group »a« and the group of inert gases the part of the group »b«, the occurrence of the latter being smaller.

The Vanadium Shortage in the Sea Water

There is, finaly, one more deviation from the rule of predominance of the partners »a«, evident in the case of vanadium in the sea water (in the earth's crust this element conforms to the rule). Vanadium occurs in sea water in a quantity which is for about 2 potencies smaller than the quantity of occurrence of its partner »b« i. e. arsenic *(As),* while in the earth's crust, according to available data, the situation is reverse. Here vanadium (partner »a«) occurs in a quantity which is for about 2 potencies larger than those of arsenic, thus conforming to the rule of predominance of elements belonging to subgroups »a«.

But whence this shortage of vanadium in the sea water, and how to explain it? At first thought one would suppose that the quantity of arsenic in sea water had been overrated owing to the fact that the akin antimony *(Sb)* is stil undetermined in sea water, so that parts of it may have influenced the available analyses relative to occurrence of *As* in sea water.

But there is not much probablity for such an explanation owing to the fact that the element which occurs in a small quantity (e. g. *Sb)* is not likely — at the chemical analisis — to influence much the result relative to the akin element occurring in a far larger quantity (e. g. *As)*, while the reverse case is a normal and regular appearance.

There is another explanation, very curious, but risky as well. Well conscious of its venturesomeness, we give it here because it is interesting.

Some indications show that the quantity of vanadium in sea water has grown smaller in comparison with its earlier occurrence. It has been found that vanadium constitutes an essential part of the blood colouring matter of some older forms of marine animal life, as for instance the ascidians (M. Henge, 1913; Hecht, 1918; M. Azéma, and H. Pied, 1930; J. Cantacuzène, and A. Tchekirian, 1932; A. P. Vinogradoff, 1932) and of some much older forms, as for instance the holothurians (Phillips, 1918 — quoted from H. W. Harvey, 1928, p. 28 and from S. Miholić, 1934, p. 159).

In addition to this we may suppose that there were periods in our earth's past when this element was more intensively utilized by organisms in their process of exchange of matter than it is being utilized to-day. The same concerns plants also. Vanadium is very frequently being found in the ash deriving from fossile plants. According to H. E. Crossley (1946), vanadium does occur in considerable quantities in the coals mined in British collieries. — It may be assumed that the plants which were tranformed into coal, had accumulated vanadium as a matter essentially needed for their normal growth.

Vanadium has also been detected in large quantities in the ash of the Argentine lignite (F. Heinrich and F. Petzold, 1932).

Agreeing with R. J. Mayer (1932) we may generally take the occurrence of vanadium in fossile plants as a normal phenomenon.

But let us return to the marine organisms containing vanadium in their pigment.

When, during the process of evolution, various kinds of chromoproteids developed within groups of organisms in sea water, it happened in the course of the process that different elements entered such large proteidic molecules, viz.:

Iron *(Fe)* into haemoglobin (verterbrata, some worms, etc.), into chlorocruorine (anelides), and into haemo-erythrin (sipunculus):

Copper *(Cu)* into haemocyanine (molusca; crabs: palinurus and limulus; some arachnoids);

Vanadium *(V)* into ascidians and holothurians, where it plays the part of the respiratory pigment like the earlier mentioned colouring-matter (P. Rondoni, 1942).

What was then to determine which of the heavy metals shall enter the prosthetic group of proteids at the time of development of the above and other chromoproteids containing heavy metals? The determining factors were, evedently, the chemical properties of the respective metal, its fitness for passing from one degree of oxidation to the other, its affinity towards carbonic compounds, etc., but also the fact whether the outer medium, i. e. the sea water, contained adequate quantities of that element.

We find now that these metals occur in the sea water in following quantites, measured in gramatoms p/t:

Fe . . . . . . $3{,}6 \times 10^{-4}$
Cu . . . . . . $1{,}57 \times 10^{-4}$
V . . . . . . $6{,}0 \times 10^{-6}$

It is visible from this comparison that the quantities of iron and copper in the sea water belong to the same set, while vanadium, standing apart, occurs in quantities which are for about 2 potencies smaller in comparison whith the first two elements.

This may suggest that, in the course of time, the quantity of vanadium in sea water had grown smaller in some way, i. e. that the major part of vanadium in sea water had been precipitated.

But how could this have happened?

The compounds of vanadium are easier soluble in more acid mediums. According to existing opinions the original ocean, before a larger influx of inland waters had taken place, showed an acid reaction in contrast to the slightly alcalic one shown in our days (L. K. Blinoff, 1946).

Vanadium occurs in different degrees of oxidation. When 5-valent (viz. in its highest valence) it appears to be an acid, and better soluble, having a high »ionic potentiality« (V. M. Goldschmidt), while when 2- or 3- valent, thus having a lower »ionic potentiality« (radius of the ion multiplicated by valence), vanadium is almost insoluble or hardly soluble.

The properties of the Archaean or Paleozoic ocean were then such that the sea water of that time — being more acid — contained larger quantities of dissolved vanadic ions, all this in accordance with the rule of predominance of elements of the group »a«.

The precipitation of vanadium in sea water was, perhaps, due to two factors, firstly, to progressive growth of alkalinity of sea water, this resulting in diminishing the solubility of vanadium, and, secondly, to appearance of factors preventing vanadium to be oxidated into its 5-valent from. The latter case may have happened when there was no more free oxygen (O_2) in sea water, which is an essential factor in the process of oxidation.

Conditions found in the Black Sea and in some of the fiords show that cases of absence of free oxygen (O_2) still occur, and there, in consequence, various substances cannot be oxidated. Organic sulphur (S), for instance, is not being transformed into SO_4'' but reduced to hydrogen sulfid (H_2S). Along with this process the burning of organic sediment fails to take place, and slime rich with organic matter — sapropel — settles on the sea bottom. The striking feature of this slime is its abundance with some metallic elements, vanadium also included (Kalle, op. cit., page 137). A. D. Arhangelski and E. V. Kopčinova found, for instance, the slime deriving from greater depths in the Black Sea to be rich with organic matter and to contain 0.01—0.06% V_2O_5 (quoted from S. Miholić, 1935; p. 159).

According to more recent data, the formation of mineral oil is being brought into connection with these sapropelic layers in the following way (after A. Treibs, 1940): sulphuric bacteria, by taking completely away the oxygen from organic compounds, produce free CO_2, whilst the remaining organic matter changes into hydrocarbons.

Owing to the shortage of O_2 in sea water, the precipitation of vanadium is intensively taking place, as said above, on isolated ocean areas only. But, according to H. Schmidt and K. Krejci-Graf (1935), there were so called »sapocratic« periods of the oceans in the past, when conditions prevailed similar to those existing now in the Black Sea, with analogous accumulation of sediments.

During these periods the one time abundant quantity of vanadium in sea water was caused to precipitate. The same thing happened, probably, to some elements of the subgroup V a (Nb and Ta).

Further agreement with the above account is noteworthy. Fr. Tućan (1930), dealing with geochemistry of vanadium, stated the presence of vanadium in asphalts, and in sandstone, expressing the opinion that it probably entered the sediments through living matter.

It is unlikely that the ascidians and the holothurians were the only organisms to supply these sediments, since they alone, however numerous, could not influence the formation of strata!

R. L. Mayer (op. cit).) finds mineral agglomeration of organic origin, containing vanadium, to be particularly interesting. In the residue of many kinds of burnt mineral oil, especially of the heavy ones, and of asphalts, V_2O_5 has been found in a striking quantity (De Golyer, 1924).

By analyzing the ash of Argentine and Venezuelan mineral oils, vanadium has been found in the former for about 38.2 p.c. and in the latter up 45.38 p.c. The Peruvian asphalts, rich with sulphur (!), contain plenty of vanadium as well (Hewett, 1909).

The conclusion may therefrom be deduced that the life which existed on our Earth in bygone ages was depending upon the utilization of vanadium as an agent in the process of exchange of matter in the same way as it now depends upon *Fe*, or *Mg*.

Caused by changes of physical and chemical conditions, the vanishing of vanadium from sea water took place, or, precisely said, its quantity probably fell to 1/50 or even 1/100 (and, perhaps, to a still smaller part) of the original amount.

These changes presumably caused whole groups of marine animals and, possibly, of plants likewise to disappear. The rare animal forms that to-day still utilize vanadium for the purpose of exchange of matter, are likely but a small remainder of the one time profuse marine organisms of that kind. They are probably owing their prolonged existence to their extraordinary high adaptability to the new conditions which took place some time.

Is it possible, perhaps, to bring into connection the sudden disappearance of different marine organisms, some time profusely represented, such as trilobites, nummulites, and others, with the similar changes of composition of the sea water pertaining to onetime seas?

According to S. Miholić (1934) the quantities of vanadium determined in various biogenetic occurrences show that their maximal values appear with the strata of Upper Cretaceus and Tertiary.

It is very interesting, indeed, that to the same period belong the last occurrences of some groups of marine organisms which do not appear in later strata.

It is evident from Tables 7 and 8 that all the couples of elements show an obvious predominance of the partner »a« over the partner »b«, usually for 2—3 potencies, with the exception of the couples *Zr* — *Sn* (group IV) and *Ta* — *Bi* (group V) in the earth's crust, where the predominance of the partner »a« is very small: less than 1 potency, as from available data.

Could not we expect, perhaps, that some new, as yet unknown data might produce changes in the ratios between the elements of the couples *Ta-Bi* and *Zr-Sn,* in favour of their partners »a«.

This rule of predominance of subgroups »a« may be taken as a further extension of the group rule concerning the functional connection between the occurrence of elements and their atomic number. It may be seen that this rule is consistently valid within each of the groups (according to Werner's conception of groups, — Table 3). If we look broadly upon whole groups, after Mendeleeff and Antropoff (head elements, plus subgroup »a«, plus subgroup »b«) — judging, of course, from available data—then the mentioned deviations from our group rule come into view. But if, finally, we extend our reviewing to the whole system of elements regarding the functional connection between the occurrence of elements and their atomic number, the result would be a large number of exceptions, i.e. the review would be a failure.

GENERAL CONCLUSIONS

The literature has thus far recorded two rules concerning the occurrence of elements in the earth's crust (Goldschmidt, op. cit., Eggert-Hock, op. cit.):

a) The increase of the atomic number of elements in the earth's crust is generally followed by the decrease of occurrence;

b) The elements with even atomic numbers almost regularly occur in larger quantities than the neighbouring ones with uneven atomic numbers (Oddo — Harkins rule).

But these rules do not apply to a considerable number of cases, as evident by a mere glance at the Figure 2.

The literature consulted by the author of this paper gives no review of this kind that would cover the elements which occur in the sea water.

It is, therefore, the purpose of this paper to give an arrangement of elements occurring in the sea water, not according to the criterion hitherto applied, viz. by decreasing quantities only, but by increasing atomic numbers. The occurrence of the elements in the sea water, as visible from Fig. 1, bears resemblance with the conditions existing in the earth's crust, i.e. the occurrence decreases as the atomic number increases.

A further resemblance in the conditions consists in the fact that the two rules stated for the earth's crust, (a) concerning the decrease of occurrence being inversely related to the increase of the atomic number, and, (b) the Oddo-Harkins' rule, in a great many cases do not apply to the sea water either.

This paper represents, then, the first attempt to arrange and review the occurrence of elements in the sea water as it has been already done for the earth's crust, not for all elements taken together, but separately for different groups of the periodic system of elements.

By the application of the criterion of aperiodicity, the rule Oddo-Harkins comes clearly into view, whilst the rule concerning the decrease of occurrence is hardly recognizable, owing to the interference of considerable deviations and oscillations, associated with this way of observation.

But if the atomic number of elements (abscissa) is taken for the criterion, the periodicity of the system of elements should still be taken into account (Mosley's discovery does not reduce the value of the Mendeleeff classification!). This is provided by handling the elements separately by groups of the periodic system of elements instead of taking all the elements together).

Here, then, the application of the Oddo-Harkins rule was excluded, but another one, concerning the functional connection between the occurrence and the atomic number (the group rule) is emerging conspicuously, bearing sings of a regularity by which each group of the periodic system of element's possesses its own characteristic features. The available data for sea water are sufficient to-day to verify the evident consistence with the above rule for at least ten groups or so (groups taken according to Werner's conception of the periodic system).

There are groups where the course of decrease is rapidly following the increase of the atomic number, while the slope is more gentle with some other groups, and in the case of the group III a the decrease of occurrence is equal to zero, or there is even an increase of occurrence following the rise of the atomic number. Similar conditions as to the occurrence of elements have been found to exist also in the earth's crust, but it should be pointed out that the run of lines relative to single groups show by far more regularity in the case of the sea water than in the case of the lithosphere.

A phenomenon called the rule of deflection, taking place almost with every group curve, has been disclosed, consisting in the fact that the run of the curves is being deflected, this tending to hinder their further fall and causing them to run more horizontally, or even to bend upwards. This deflection usually appears when the element of the fiftih period of the respective group is reached, owing to the fact that the quantities of the elements of the sixth period show a relative increase.

The phenomenon of the decrease of elements belonging to the seventh period has also been stated, basing upon the observation that the elements of this period, i.e. the last members of some group curves, owing to their small occurrence, cause a rapid downward deflection of curves.

Conditions here are not so clear as in the case of the rule of deflection, because the group of actinides is superposing its still unclarified relations, but indications seem to exist that this group conforms to the Oddo-Harkins rule, e.g. thorium *(Th)* and uranium *(U)*, having even atomic numbers and occurring in greater amounts.

It results from the foregoing that the old rule of decreasing occurrence with the atomic number increasing (for all elements taken as a whole) is not applicable here, but the rule of functional connection between the occurrence of elements on the one and the increase of the atomic number on the other hand, operating within single groups of the periodic system.

This rule has a wider range in comparison with the old one, as it includes also the cases where the occurrence does not decrease with the atomic number increasing. While there was a large number of exceptions with the old rule, which actually was but a gross approximation, our group rule shows almost no exceptions at all (a few first head elements being the rare ones) and it should be given a prominent place.

In short, by limiting the review of occurrence and of the atomic numbers to elements of but one group (taking the system accordnig to Werner), an obvious regularity of relations in the above mentioned characteristics of elements becomes perceptible.

By extending the review in a way to include the whole group according to Mendeleeff or Antropoff (head elements, plus subgroup »a«, plus subgroup »b«), the predominance of the occurrence of the subgroups »a« over the corresponding subgroups »b« becomes manifest, with several exceptions concerning both the water and the earth's crust.

By taking, finally, the system of elements as a whole, a great many exceptions appear.

If a consistent regularity is to be attained, the rule of relationship of occurrence of elements should be applied to groups of the periodic system (taking the system as modified by Werner). Thus we arrive at the group rule of functional relationship between the occurrence of elements and their atomic numbers, or simply the group rule.

When applying this way of exposition, no place is left for the Oddo-Harkins' rule, with the only exception of the group III a, where the neighbouring elements appear alone next to each other.

The mutual relationship of occurrence of single elements in the earth's crust v is truly reflected by the conditions existing in

v usually

sea water, as it results from comparison, the latter usually containing smaller quantities.

When arranging the occurrence of elements in the earth's crust, we noticed the deviation of the first head elements, towards lower occurrences in the case of all groups, except oxygen which shows a higher value.

There is more regularity in this regard in the sea water, since the first members of the groups III, IV, and V *(B, C, N)* do not show such shortages. There is likewise no irregularity with the group IV b in the earth's crust, whilst no such irregularity seems to exist in the sea water.

Two alternatives are possible: (1) that the analyses and data for the earth's crust given in the literature are proper and accurate, but owing to some peculiar fact, and wholly independent of their occurrence in the earth's crust, the elements in the sea water range according to their occurrence in clearly expressed series, standing in an obvious connection with their atomic weights and/or with their atomic numbers, taken groupwise according to the Mendeleeff classification; (2) that the hitherto made estimates of the occurrence of some elements in the earth's crust are incomplete and that their revision is likely to be expected as required by our curves. This applies particularly to the elements *Sn* and *Ge*.

Basing upon obvious regularities deriving from our way of observation, and from parallelism of conditions found to exist both in the sea water and in the earth's crust, we are likely to be able to make some anticipations with regard to the occurrence of single elements still undetected in sea water. This applies particularly to the elements *Ge, Sb, Cd, Cr,* and *W*.

A further regularity has been found consisting therein, that the elements belonging to the subgroup »a« of the periodic system, are occurring in larger quantities than their corresponding partners, i. e. elements belonging to the subgroup »b« of the same period (rule of predominace of the subgroup »a«).

The result of examination of the available data, and of recent experiments, suggest that, by further investigation, a change is likely to be expected of the ratio between the quantities of *Hf* and *Pb* in favour of the first element, as it has been already confirmed by some recent data resulting from experiments. It results further that the ratio between the quantities of elements in the couples *Zr-Sn* and *Ta-Bi* — so far as it concerns the earth's crust — has most probably been established on estimates which seem to be too high for *Sn* and too low for *Ta*, with regard to their respective partners.

This conclusion, drawn from examination of *Zr-Sn*, with regard to the rule of predominance of the partner »a« is in accordance with the results of examination of the structure of group curves as far as it concerns *Sn* and *Ge* both in the sea water and in the earth's crust.

Basing upon the structure of the group curves for the groups VII and VIII as well as upon the rule of predominance of the subgroups »a«, the observation has been made that the subgroup *Mn* (subgroup VIIa) is more related to the group VIII than to the group VII. The subgroup *Mn* has been consequently placed into the group VIII with respect to its occurrence, and this subgroup, together with the subgroup *Fe* form the group $VIII_1$, while the subgroups *Co* and *Ni* form the group $VIII_2$.

The probability has been deduced that at some time in the past vanadium disappeared from the sea water, where it once used to occur in quantities exceeding the actual ones.

The curves of occurrence of elements according to the groups of the periodic system of elements show their individuality nad regularity (the group rule). But they are subject to higher rules: to the rule of the deflection of curves, and to the rule of predominance of elements belonging to subgroups »a«. We find that these latter rules comprehend all group rules, and, mutually bound, produce together with them an orderly system of regularities which enables us to draw various conclusions.

Differing from the former rule of decreasing occurrence of elements which represents but an approximation of the qualitative character of lower utility value, the regularities exposed in this paper, namely, (1) the group rule; (2) the rule of predominance of elements belonging to subgroups »a«; (3) the rule of deflection of curves on reaching the elements of the fifth period; (4) the rule of a fall of curves on reaching the elements of the seventh period; (5) the deviation of head elements of single groups; and (6) the rule acknowledging hydrogen (*H*) as belonging to all groups as a head element; — authorize us to draw conclusions from numerical data now available, because all these rules together possess, besides a qualitative, also a quantitative value, representing together a regularity of a higher degree.

The composition of the sea water with regard to the elements was hitherto divided only into major and minor constituents. This had a practical value although the division line between the two groups was placed rather arbitrarily. *B*, *Sr* and *C* were not, until recently, placed among the principal elements, but now they are treated as such.

By reviewing groupwise the relationship of occurrence of elements, we find that there exists a regularity as to the quantitative occurrence of elements of each group of the periodic system of elements as far as sea water is concerned. This may facilitate the survey and be useful for the classification and systematization of a large number of elements already detected in sea water, to which also futher ones are likely to be added.

We expect that the rules given in this paper, as well as the conclusions drawn from them, will find useful application in the framing of working hypotheses not only where the investigation of the sea water and the earth's crust is concerned, but also when handling the »trace-elements« occurring in other regions (for example in the organisms or in the soil).

Judging from similarity of occurrence of elements in the earth's crust and in the sea water, and from given regularities which seem to be everywhere of approximately the same validity, these regularities will, most probaly, be extended to the world of organisms as well.

Several indications, noticed by the author, underlie this claim, particularly those contained in the A. P. Vinogradoff's work (1944), where data of this kind have been abundantly collected.

Considering the property of the organisms to perform biogenetic concentrations of various elements from high dilutions, it is possible to anticipate that the pictures of group curves will be characteristic for single groups of organisms, and that these curves may differ slightly from curves pertaining to the anorganic world.

By accepting the rules given in this paper as the working principle pending investigation of the biogenetic elements we arrive at a new stand-point and at a system able to produce a better review and orientation than provided by the previous division of elements into biogenetic-, nutrient-, plastic-, catalytic-, ballast-, contaminant-, trace-elements, and the like.

The application of these regularities may, at the same time, prove to be a decisive way-mark when we have to resolve in what direction and on which element of a particular group the examination should be focussed with regard to influence and rôle of elements in the organisms.

Basing on experiences acquired hitherto, we should say that the occurrence of elements, arranged in this way (by grups), constitutes a characteristic of the group in addition to other properties which are subject to change by the increase of the atomic numbers of the elements belonging to the group, e. g. the specific weight, the melting point, the boiling point, the colour, etc.

The review of the group II may be completed as follows:

Table 10

Atomic number	ELEMENT	Symbol	Atomic weight	Specif. weight	Melting point °C	Boiling point °C	Valence	Percentage in the earth's crust divided by atomic weight	Gramatoms p/t of sea water
4	Berylium	Be	9,02	1.86	1285	2970	II	$4,4 \times 10^{-5}$	
12	Magnesium	Mg	24,32	1,74	650	1100	II	$9,6 \times 10^{-2}$	$5,3 \times 10^{1}$
20	Calcium	Ca	40,08	1,54	845	1439	II	$8,1 \times 10^{-2}$	$1,02 \times 10^{1}$
38	Strontium	Sr	87,63	2,60	757	1366	II	$4,0 \times 10^{-4}$	$1,47 \times 10^{-1}$
56	Barium	Ba	137,36	3,74	710	1696	II	$3,6 \times 10^{-4}$	$4,00 \times 10^{-4}$
88	Radium	Ra	226,05	6,—	700	—	II	$8,8 \times 10^{-13}$	$1,2 \times 10^{-13}$

All regularities, and anticipations deduced from them, in the course of this study, are based upon the relationship of occurence of elements and their atomic masses. The properties of the electronic outer orbits of single elements, have been taken also into consideration. They are actually postulates of that regularity disclosed by V. Mendeleeff, who was the first to give an exact formulation of the periodic system of the elements.

In a speech delivered in Moscow during the congres held in commemoration of V. Mendeleeff, I. Noddack (1937) expressed the thought that the periodic system alone does not allow any anticipations to be made as to absolute occurrence of a certain element. — Now does not our paper offer a revision of this opinion, making posible to provide a further support, even in this field, of the genial and comprehensive conception of great Mendeleeff?

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SUMMARY

(1) An arrangement of elements occurring in the sea water hareby given with regard to their decreasing occurrence with the increase of the atomic numbers. A statement has been made that, taken in general, the occurrence of elements in the sea water and in the earth's crust bear similar features, i. e. that the existing conditions conform grossly to the rule of the occurrence decreasing with the increase of the atomic number.

(2) It has been recorded that the rule mentioned above and the rule Oddo-Harkins do not apply to a large number of elements in the sea water, as it was found to be the case with the earth's crust also.

(3) This represents the first attempt to give an arrangement of elements by their increasing atomic numbers, but keeping within the limits of single groups of the periodic system of elements. This has been done for the sea water and for the earth's crust alike.

(4) This helped to disclose the existence of regularities being characteristic for the single groups of elements of the periodic system — *the rule of the functional connection between the occurrence of elements and their atomic number,* applicable to *every group* of the periodic system of elements separately, or, abridged, *the group rule.* This again led to the elimination of numerous irregularities that appear when all the elements are taken together, in accordance with the old rule of occurrence.

(5) Owing to the scanty data available for the sea water, it has been found that at least ten groups of elements conform to the group rule (groups taken after Werner's rearrangement of the periodic system of elements).

(6) With regard to the occurrence in the earth's crust it has been found that almost all the groups conform to the group rule.

(7) Figures showing the curves of occurrence of elements by groups are disclosing a regular decrease with the increase of the atomic number, with the exception of the group III, whose curve is running almost horizontally, tending even to rise.

(8) It is characteristic for the curves of the groups that hydrogen may be taken as the starting point of almost every curve.

(9) The low occurrence of the first head members of the groups I, II, VII, and O, and the surplus oxygen in sea water are also characteristic. In the earth's crust all the first head elements (of the second period of the system of elements) appear to be deficient, with the exception of oxygen, which occurs in superabundance.

(10) The phenomenon called *the rule of deflection* has been ascertained further for almost all the groups of the periodic system, consisting in the deflection of the group curves of occurrence at the point where the elements of the fifth period are reached, and resulting in a slowing down, or even in a stop of the more or less rapid fall of the curve.

(11) A phenomenon of decreasing quantities of elements belonging to seventh period of the system of elements (elements with atomic numbers from 86 upwards) has also been noticed. This phenomenon consists in the fact that the elements of this period occur in extraordinary small quantities, thus contrasting the above rule of deflection (see point 10).

(12) A regularity called the rule of predominance of the elements belonging to subgroups »a« has been disclosed, consisting in the fact that the elements of the subgroup »a« of the periodic system (as arranged by Antropoff) are more abundant than their partners belonging to the subgroup »b« of the same group

and of the same period. The probability has been deduced therefrom that at one time the quantity of vanadium occurring in the sea water, was much larger compared with its amount at present.

(13) The ascertained regularities: the shortage of the head elements (point 9); the rule of deflection (point 10); the phenomenon of decreasing quantities of elements belonging to the seventh period (point 11); and the rule of predominance of elements of the subgroups »a« (point 12), are actually complementing the group rule. These rules apply likewise to the sea water and to the earth's crust.

The group rule, supplemented like this, is disclosing the functional connection between the occurrence of the elements and their atomic number, attaining this in some other, better, and more complete way than it was possible by applying the old rule concerning the decrease of occurrence, according to which all the elements, taken together, were simultaneously handled. Whilst the old rule had but an approximate and qualitative value, our group rule possesses, besides a qualitative, also a quantitative value, representing thus a regularity of a higher degree.

(14) Basing upon the above rules, the probability has been suggested that corrections are likely to be made as regards the quantities of some elements thus far determined in the earth's crust (*Sn, Ge, Pb, Hf* and *Nb*). It has also been found possible to anticipate the quantities of some elements occuring in the sea water, but as yet undetected there (*Ge, Sb, Cd, Cr*, and *W*).

(15) It has been pointed out, finally, that our way of reviewing the occurrence of elements by groups (replacing the old division into major and minor constituents), shows a regularity and, contributes to a systematization and a better understanding of the complex system of the basic matter in the sea water, thus facilitating the oceanographic studies concerning the chemical composition of the sea water.

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ČESTOST ELEMENATA U MORU I U ZEMALJSKOJ KORI U ODNOSU SA PERIODNIM SUSTAVOM ELEMENATA

(sa 20 grafova u tekstu)

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Kratak sadržaj

1. U ovom radu je izvršeno svrstavanje elemenata, koji dolaze u moru, po rastućem atomnom broju obzirom na čestost dolaženje pojedinih elemenata. Konstatirano je da se, općenito uzevši, čestost elemenata u moru ponaša slično kao i čestost elemenata u zemljinoj kori t.j., da postoji grubo pokoravanje pravilu opadanja čestosti s porastom atomnog broja.

2. Veliki broj elemenata u moru je kršio to pravilo (slično kao i u zemljinoj kori). Isto tako je veliki broj elemenata u moru kršio Oddo-Harkinsovo pravilo (kao i u zemljinoj kori).

3. Prvi put je primijenjeno svrstavanje elemenata po rastućim atomnim brojevima, ali ograničeno na pojedine skupine periodnog sustava elemenata. Ovo je provedeno za more i paralelno za zemljinu koru.

4. Na ovaj način se pokazalo, da postoje pravilnosti karakteristične za pojedine skupine elemenata periodnog sustava — nazvane pravilom funkcionalnosti čestosti elemenata i njihovih atomnih brojeva i to samo unutar pojedine skupine periodnog sustava elemenata, ili kraće skupinsko pravilo. Ovim postupkom je nestalo onog mnoštva nepravilnosti, koje je pratilo staro pravilo čestosti elemenata, kada se vršio pregled elemenata skupa.

5. Za more je i sada, kod manjkavih podataka kojima se danas raspolaže, konstatirano potpuno pokoravanje skupinskom pravilu kod desetak skupina elemenata (Wernerovog oblika periodnog sustava elemenata).

6. Za čestost elemenata u zemaljskoj kori je također konstatirano pokoravanje skupinskom pravilu skoro kod svih skupina.

7. Slika krivulje čestosti elemenata po skupinama pokazuje pravilno opadanje s porastom atomnog rednog broja, osim kod III. skupine, čija krivulja teče gotovo horizontalno i čak pokazuje tendenciju porasta.

8. Za krivulje skupina je značajno, da kao polazna točka skoro svake krivulje može poslužiti vodik.

9. Za morsku vodu je značajno podbacivanje količina prvog čeonog člana I., II., VII. i O. skupine, i prebacivanje količina kisika.

   U zemaljskoj kori količinom podbacuju svi prvi čeoni članovi (elementi druge periode sustava elemenata), osim kisika, koji prebacuje.

10. Prvi put je konstatirana pojava nazvana pravilom loma kod gotovo svih skupina periodnog sustava, koja se sastoji u tome da skupinska krivulja čestosti doživljava jedan lom kod elemenata 5. periode, koji usporuje, a nekada čak potpuno zaustavi padanje krivulje.

11. Uočena je nadalje pojava opadanja čestosti elemenata 7. periode sustava elemenata (elementi sa atomnim rednim brojem od 86 naprijed). Ova se pojava sastoji u tome, što elementi ove periode pokazuju izvanrednu nisku čestost. Ova pojava ima obrnuto značenje od gornjeg pravila loma (10. točka).

12. Prvi put je nadalje konstatirana pravilnost, nazvana pravilom nadmoćnosti elementa »a« podskupina, koja se sastoji u tome, da svaki elemenat »a« podskupine periodnog sustava (oblik po Antropovu) preteže svojom čestosti nad svojim partnerom t. j. elementom iz »b« podskupine, iste skupine, iste periode. Odavle je izvedena vjerojatnost, da je vanadij svojedobno dolazio u moru u mnogo većoj količini, negoli se danas tamo nalazi.

13. Iznesene pravilnosti: odstupanja čeonih elemenata (toč. 9), pravilo loma (toč. 10), pojava opadanja količina elemenata

VII. periode (toč. 11), te pravilo nadmoćnosti elemenata »a« podskupina (toč. 12) — u stvari služe, kao prilog skupinskom pravilu (toč. 4), čija su stvarna dopuna. Ova prvila a vrijede kako za more, tako i za zemaljsku koru.

Ovako kompletirano skupinsko pravilo izražava funkcionalnu vezu čestosti elemenata s njihovim atomnim brojem na jedan drugačiji, viši i potpuniji način, nego staro pravilo o opadanju čestosti, koje je istodobno obrađivalo sve elemente skupa. To staro pravilo je bilo aproksimativnog i kvalitativnog značaja.

Naše skupinsko pravilo ima osim kvalitativnog također i kvantitativni značaj, pa predstavlja pravilnost višeg stupnja.

14. Na temelju gornjih pravila iznesena je vjerojatnost, da će se moći vršiti neke korekture u pogledu dosada utvrđenih količina dolaženja nekih elemenata u zemljinoj kori (Sn, Ge, Pb, Hf, Nb i Ta).

    Iznesena je mogućnost predviđanja količina u kojima neki elementi, koji tamo još nisu dokazani (Ge, Sb, Cd, Cr i W), dolaze u moru.

15. Ukazano je na to, da je u oceanografiji, i to u proučavanju kemijskog sastava morske vode, umjesto dosadanjeg pomagala diobe na major i minor constituents, ovim pregledom čestosti elemenata po skupinama, dobivena jedna zakonitost, koja će pomoći unijeti red, sustav i bolje razumjevanje složenog sistema osnovnih tvari u moru.

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Tisak: Gradsko štamparsko poduzeće „Ante Jonić" — Split