COMITÉ DE CHIMIE DE LA MER

Président : Prof. MALDURA (Italie)

AN ASPECT OF GEOCHEMICAL SIGNIFICANCE OF SEA WATER AMONG THE NATURAL WATERS

by Miljenko BULJAN

During our earlier work carried out to determine the influence exerted by sea water on the chemical composition of some subsurface and surface water types of the yugoslav Adriatic littoral, we have usefully applied the ratio of SO_4^{2-}/Cl concentration as found in natural water (BULJAN, 1955).

Owing to the wide range of sulfate and chloride concentrations occurring in natural waters, the ratios in the graphs are expressed by the function : $\log [Cl^-] = f (\log [SO_4^{2-}])$

The water types occurring in Croatia are dealt with in the first place, and we have found the available chemical analyses made by the lately deceased explorer of Yugoslav mineral waters S. MIHOLIC, the geochemist, as well as those by MIHOLIC and TRAUNER, particularly useful. We have also made use of some earlier made analyses involving the water types occurring in the littoral, as well as of our own analyses made for the purpose of the present paper. The method applied to determine the chloride and sulfate contents was the same as previously adopted by us (BULJAN, op. cit.). The data referring to other water types have mainly been obtained from the works of CLARKE (1924), KALLE (1942) and SAHAMA and RANKAMA (1950). (All the data are given in tab. 1 [1].)

Rain Water ("K" Water).

In graph. 1, most of the water types fall into the group labelled "K". Rain water, as well as a series of water types deriving from rivers, lakes and springs, including also mineral springs, belong to this group. Through a sinusoidlike curve the "K" group joins brackish water types and, finally, sea water too. Rainwater types are found on the left-hand side of the graph. The farther from the sea the places of its origin, the purer the water type (e.g. Kearney 12 situated 1 400 kilomètres from the seaboard). The nearer the sea the places of water origin are situated (Split 31), the higher the probability of occupying the right-hand, i.e. the marine side of the graph.

The water coming from the rivers Krka (15), Jadro (39), Zrmanja (21), Mississipi (36), from three lakes in Switzerland (5, 25, 41), and from some mineral springs in Yugoslavia belong to the "K" group of water types. These water types easily and naturally join the sea water through the above-mentioned "sinusoid". We are not in the position to explain why a number of mineral water types from Northern Croatia and the Littoral also lie along this curve (graph 2). Here are some such water types: Sv. Ivan Zelina (24), Stubicke Toplice (22), Topusko (27), Sv. Jelena (35), Varazdinske Toplice (48), Ulcinj (49), Mokosica (54), Monastery Sulphur Spring at Split (55), and Split Baths Sulphur Spring (53, 57).

(1) We thank for kind cooperation to Mg. pharm. Dalibor Bonacci, from Institute for Hygiene, Split, who supplied the data.

Nº	Origine of water (MW = mineral water spring)	Cl^- g / kg	SO_4^{2-} g / kg	SO_4^{2-}/Cl^-	Literature
1	Eye water Srebrenica, M.W.	0,0012	3,809	$3,17 \times 10^{3}$	14
2	Bench Spring, Yellowstone, M.W.	0,0001	0,138	$1,38 \times 10^{3}$	17
3	Devis Inkpot, Yellowstone, M.W.	0,006	2,366	$3,95 \times 10^{3}$	17
4	Slana Jaruga	0,011	1,341	$1,22 \times 10^{2}$	3
5	Lac Noire, Swiss	0,0015	0,104	$6,72 \times 10^{1}$	17
6	Lesce, M.W.	0,0035	0,147	$4,20 \times 10^{1}$	15
7	Ivanovo Vrelo, Daruvar M.W.	0,0035	0,057	$1,74 \times 10^{1}$	15
8	Antunovo Vrelo, Daruvar M.W.	0,0035	0,058	$1,66 \times 10^{1}$	15
9	Semnica, M.W.	0,0025	0,043	$1,64 \times 10^{1}$	15
10	Tuhelj-Dada, M.W.	0,0025	0,039	$1,51 \times 10^{1}$	15
11	Rimske Toplice, M.W.	0,0018	0,027	$1,49 \times 10^{1}$	10
12	Rain water-Kearrney (1 400 km from coast)	0,00014	0,002	$1,43 \times 10^{1}$	6
13	Krapinske Toplice, M.W.	0,0029	0,041	$1,40 \times 10^{1}$	15
14	Rain water-Washington (200 km from coast)	0,0007	0,0095	$1,36 \times 10^{1}$	6
15	Krka river, Jugoslavia	0,0047	0,063	$1,34 \times 10^{1}$	this paper
16	Tuhelj-bara, M.W.	0,0030	0,038	$1,28 \times 10^{1}$	15
17	Velika Juzna, M.W.	0,0024	0,030	$1,25 \times 10^{1}$	15
18	Sutinske Toplice, M.W.	0,0027	0,033	$1,21 \times 10^{1}$	15
19	Harina Zlaka, M.W.	0,0033	0,040	$1,18 \times 10^{1}$	15
20	Dobrna, M.W.	0,002	0,023	$1,16 \times 10^{1}$	10
21	Zrmanja river, Jugoslavia	0,0034	0,034	$1,00 \times 10^{1}$	this paper
22	Stubicke Toplice, M.W.	0,0096	0,085	$8,54 \times 10^{0}$	15
23	Kamena Gorica, M.W.	0,003	0,025	$8,28 \times 10^{0}$	15
24	Zelina, M.W.	0,007	0,050	$7,07 \times 10^{0}$	15
25	Lac Taney, Swiss	0,0019	0,012	$6,08 \times 10^{0}$	17
26	Velika, Sjeverno vrelo, M.W.	0,0048	0,028	$5,80 \times 10^{0}$	15
27	Topusko, M.W.	0,019	0,108	$5,54 \times 10^{0}$	15
28	Toplicica-Gotalovac, M.W.	0,0034	0,016	$4,70 \times 10^{0}$	15
29	Sv. Jana, M.W.	0,0029	0,011	$3,72 \times 10^{0}$	15
30	Rain water-Münchenberg (400 km from coast)	0,0037	0,012	$3,23 \times 10^{0}$	6
31	Rain Water-Split (on coast)	0,0054	0,017	$3,18 \times 10^{0}$	3
32	Sokoloviceva banja M.W.	0,0052	0,016	$3,07 \times 10^{0}$	12
33	Fojnica, M.W.	0,0039	0,012	$3,01 \times 10^{0}$	13
34	Kadijina banja, M.W.	0,0055	0,015	$2,67 \times 10^{0}$	12
35	Sv. Jelena, M.W.	0,066	0,176	$2,67 \times 10^{0}$	15
36	Mississippi river	0,0103	0,026	$2,47 \times 10^{0}$	17
37	Djakovacka Breznica .M.W.	0,010	0,024	$2,34 \times 10^{0}$	15
38	Medijske Toplice, M.W.	0,0019	0,0038	$2,00 \times 10^{0}$	10
39	Jadro river, Yougoslavia	0,0071	0,012	$1,73 \times 10^{0}$	this paper
40	Varazdinske Toplice M.W.	0,082	0,141	$1,72 \times 10^{0}$	15
41	Lac de Champex, Swiss	0,0026	0,0031	$1,19 \times 10^{0}$	17
42	Vretenica (Krk) M.W.	0,016	0,018	$1,15 \times 10^{0}$	10
43	Lipik, M.W.	0,395	0,246	$6,22 \times 10^{-1}$	15
44	Slatina Radenci M.W.	0,463	0,282	$6,08 \times 10^{-1}$	16
45	Caspian Sea	5,42	3,050	$5,62 \times 10^{-1}$	1
46	Lasinja, M.W.	0,724	0,281	$3,88 \times 10^{-1}$	15
47	Solana Ston, brine	180,0	47,916	$2,66 \times 10^{-1}$	this paper
48	Istarske Toplice, M.W.	1,588	0,411	$2,57 \times 10^{-1}$	15
49	Ulcinj	2,051	0,499	$2,43 \times 10^{-1}$	10
50	Kara Bugaz	118,30	22,60	$1,91 \times 10^{-1}$	7
51	Jordan river (Palestine)	3,192	0,556	$1,74 \times 10^{-1}$	17
52	Jamnica, M.W.	1,830	0,277	$1,51 \times 10^{-1}$	15
53	Split, Bath (a)	9,99	1,441	$1,44 \times 10^{-1}$	2
54	Mokosica	7,232	1,038	$1,43 \times 10^{-1}$	15
55	Split, Monastery Spring	11,02	1,546	$1,40 \times 10^{-1}$	15
56	Adriatic Sea (10 Nm SW off Vis Island)	21,34	2,963	$1,39 \times 10^{-1}$	3
57	Split Bath (b)	16,56	2,280	$1,38 \times 10^{-1}$	2
58	Igalo vrelo	1,080	0,148	$1,37 \times 10^{-1}$	x)
59	Adriatic Sea (30 Nm SW off Dubrovnik)	21,42	2,945	$1,37 \times 10^{-1}$	3
60	Ston Vrelo	1,002	0,131	$1,31 \times 10^{-1}$	this paper
61	Zakucac	2,805	0,338	$1,20 \times 10^{-1}$	15
62	Vrnjacka Banja	0,034	0,0012	$3,52 \times 10^{-2}$	1
63	Novi Sad	0,320	0,0075	$2,34 \times 10^{-2}$	9
64	Stari Becej	0,330	0,0054	$1,64 \times 10^{-2}$	9
65	Vukovar	0,192	0,0014	$7,30 \times 10^{-3}$	9
66	Prigrevica	1,629	0,0093	$5,74 \times 10^{-3}$	9
67	Sisak	0,926	0,0046	$5,06 \times 10^{-3}$	9
68	Precec (Dugo Selo)	1,137	0,005	$4,40 \times 10^{-3}$	15
69	Dead Sea	141,8	0,496	$3,52 \times 10^{-3}$	17
70	Apatovac	1,366	0,0031	$2,27 \times 10^{-3}$	15
71	Bujavica	0,366	0,00073	$2,00 \times 10^{-3}$	9
72	Sisak	0,930	0,00087	$9,37 \times 10^{-4}$	9
73	Sisak	3,585	0,0029	$8,10 \times 10^{-4}$	15
74	Caprag	0,602	0,00035	$5,90 \times 10^{-4}$	9
75	Slankamen	4,119	0,00033	$8,01 \times 10^{-5}$	9
76	Brine Abilene (USA)	110,02	0,003	$2,73 \times 10^{-5}$	17
77	Moulay Yacoub (Maroc)	17,146	0,001	10^{-5}	5
78	Paklenica	1,686	traces	10^{-5}	9
79	Prigrevica	1,571	traces	10^{-5}	9
80	Vuckovec (Cakovec)	1,146	traces	10^{-5}	15

TABLEAU I

Although purely continental according to the place of their origin, these types of water must be influenced by a factor causing their geochemical character to ressemble that of the sea water. It is interesting to note here what M.P. Tolstoy says in this connexion : "Mineralization and formation of mineral waters are greatly influenced by the sea water of pristine origin".

All the water types mentioned above are situated within *their natural bounds*, i.e. between the rain water and sea water types (graph 1).

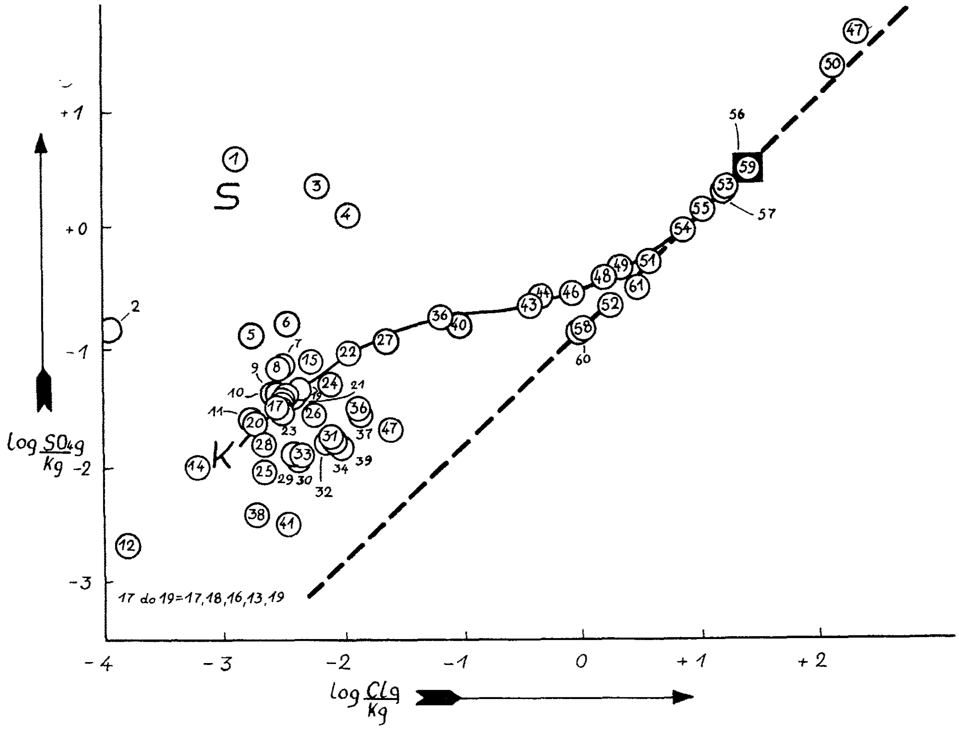

Fig. 1. — *The rain type* (K), *the marine type* (M) *and the sulphate type* (S) *of natural waters. The points n*os 59 *and* 56 *represent the Sea water. For other points consult the tab. I. or the text.*

Marine (or " M ") Water Types.

As evident from graph 1, a number of water types are located in the vicinity of the sea water owing to their SO_4^{2-}/Cl^- ratios, but differ from the latter in their salinity. We have named such waters Marine Water Types since they may, to some extent, be considered an outcome of a mixture of rain water with the sea water (Split Baths Sulphur Spring 53, 57, Monastery Sulphur Spring at Split 55, Mokosica 54, Zakucac 61, Igalo 58, Ston 60), or a result of washing down of the residual salt left behind by the ancient seas in the corresponding geological strata (e.g. the River Jordan, (Palestine) 51, and perhaps the Spring Jamnica, 52).

All these water types and some others, too, are grouped along the line (dashed diagonal) whose equation is the following :

$$\log [Cl^-] = \log]SO_4^{2-}] + 0{,}8556.$$

This « sea line » becomes particularly significant by representing the lower limit of the value log $]SO_4^{2-}]/]Cl^-]$ for any natural water at a normal redox potential whereby aeration and the presence of free oxygen are meant (graph 2). This is quite evident if we bear in mind that SO_4^{2-} present in marine water types cannot be lost as a result of reduction process under such condition. As substantiated by the data given in this paper covering 80 water types, this rule has no exception.

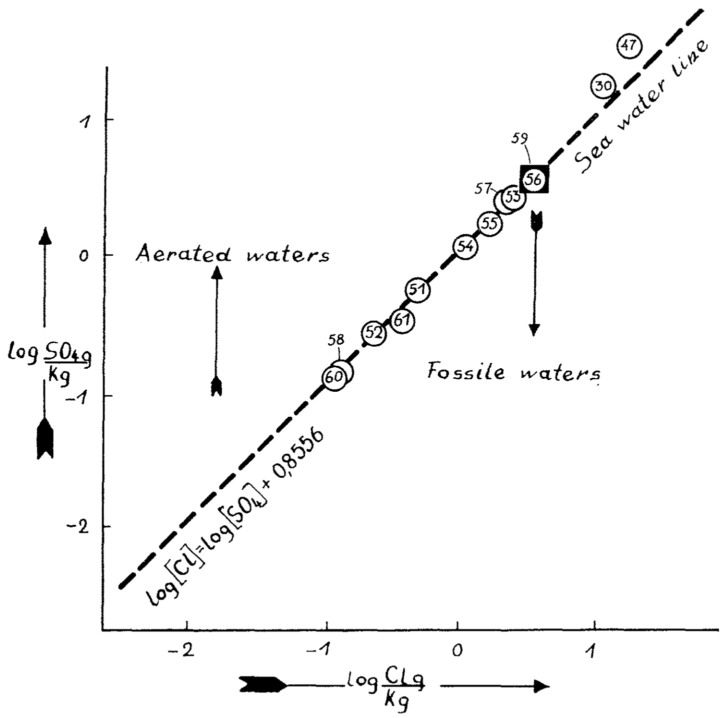

FIG. 2. — *The marine type of waters. Dashed line represents the ratio* SO_4^{2-}/Cl^- *similar to that of sea water. The equation of the line is given. For the meaning of the numbers see the tab. I.*

This "sea line" can be much helpful as a means in finding out whether a water type had, in the course of its history, a period of low redox potential usually caused by biological factors.

It seems, however, that two facts must not be disregarded in this natural grouping of water types requiring broad geochemical views.

1/ The sea water is the natural and basic water type, widely spread, and quite outstanding in its richness in mineral salts; it has left many traces ashore, even in the rocks and springs situated far inland; it is of an extremely old origin.

2/ Rain water is also a natural, to some extent everywhere present water type, widely spread, conspicuously deficient of salts, considerably dynamic, and of most recent origin.

Sulfate (or " S ") Water Types.

There are two additional water groups lying completely apart from the above-mentioned lines, i.e. the " sea line " and " sinusoid " line.

A number of water types can be found in the left upper corner of graph 3. Their principal characteristic consists in their high values of the $[SO_4^{2-}]/[Cl^-]$ ratio. Slana Jaruga in the vicinity of Sinj (4) is an example of such water types. It abounds in sulfate (therefore it is marked "S"), and it is poor in chloride. Some water types, e.g. Ocna Voda Spring in the vicinity of Srebrenica (1), Bosnia. Devils Inkpot (3), and Bench Spring (2) in the Yellowstone Park are somewhat related to it. The Lac Noir (5) and Vrelo Lesce (6) water types represent intermediary ones lying between rain water on the one hand sulfate water on the other hand.

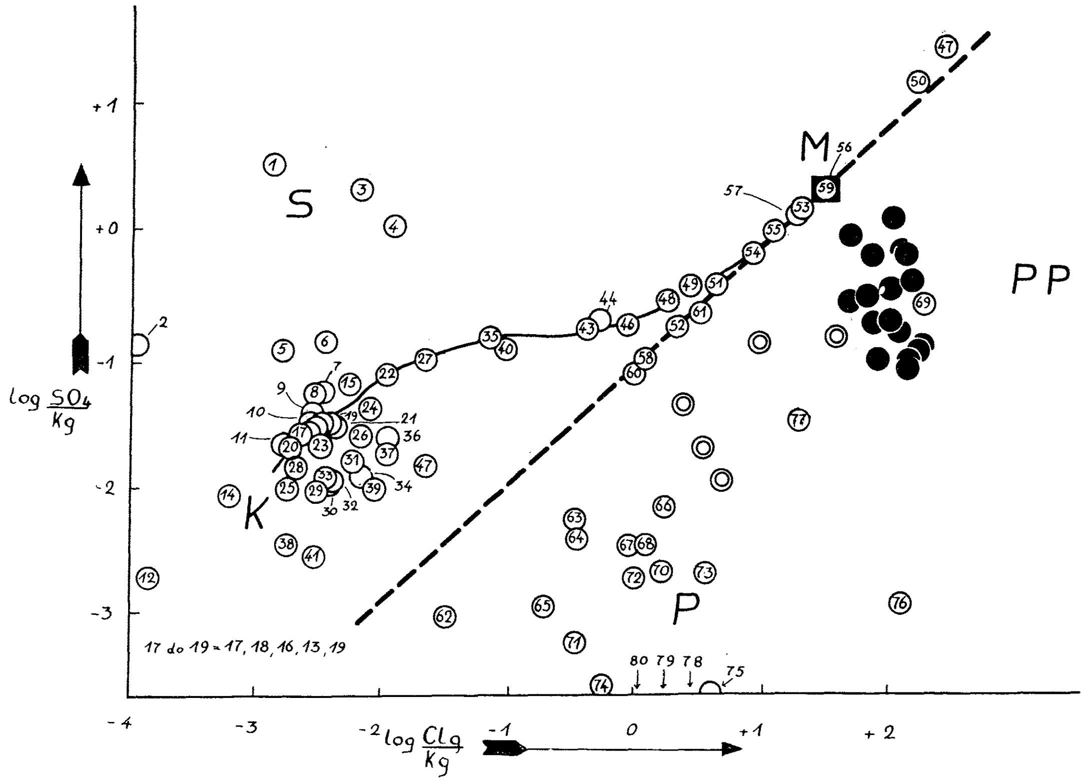

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Fig. 3. — *Together with marine* (M), *rain* (K), *and sulphate* (S) *types of water here are representeted fossile* (connate, petroleum) *waters* (P and PP) *gathered under the dashed line which has the equation log* $[Cl^-] = \log [SO_4^{2-}] + 0{,}8556$ *and goes through the sea water point. Full points on the right hand side* (PP) *represent petroleum waters from "proved oil fields" in Near East* (unpublished data). *A similar case is with the waters represented with the double circles. P waters* (down in midle) *represent various fossile waters mostly from Yougoslav oil fields area.*

Petroleum (or Fossile) Water Types (or " P " Water Types).

Another natural water group is shown in graph 3. Its water types lie below the diagonal line owing to their $[SO_4^{2-}]/[Cl^-]$ being lower than the sea water one. We shall find here a number of water types classified by Miholic as iodious ones. This type of water often contains the same concentration of sulfate as some " K " types of rain water, but it unmistakably differs from them by their higher concentration of chlorides. As shown in Graph 3, these " P " water types lie apart from the "M" water types owing to their low $[SO_4^{2-}]/[Cl^-]$ values.

By means of diagrams contained in the present paper the two water groups can then easily be told one from the other.

The fossile water types have developed either from " M " water type or from the intermediary " K-M " one through the process of withdrawal of water from circulation, stagnation, and loss of sulfate as a consequence of biological factors. The origin of this water type, is therefore, frequently connected with the formation of mineral oil.

The waters from the following springs and borings belong to the above group : Novi Sad (63), Stari Becej (64), Apatovac (70), Vukovar (65), Caprag (74), Sisak (73), Bujavica (71), Slankamen (75), Vuckovac (80), Paklenica (78). It is interesting, no doubt, that the above-mentioned representatives of the "P" water group are situated in areas where mineral oil is found. The waters of this group often happen to be in the closest vicinity both geographically and in the graph (Sisak-Caprag, etc.).

Discussion.

Juvenile water types have so far not been mentioned in the present survey owing to their rare occurrence in Yugoslavia (Lipik baths only according to MIHOLIC). On the basis of an as yet uncomplete collection of data, however, we have noticed that the position of geyser water types, i.e. water types that are in part composed of juvenile water, lies somewhere below the "sea water line" (in one such case the position is much higher, among gypsum water types), but some of the geyser water types occupy a position roughly corresponding to the « sea water line » [e.g. the waters belonging to New Zealand geyser Te Tarata and Otu Kapuarangi (CLARKE, 1924) with a SO_4^{2-}/Cl^- ratio amounting to 0,137 and 0,142 respectively!]. It may be a premature conclusion, however, that our graph suggests a close genetic connexion between the sea water and juvenile water types. Although the latter are mentioned only parenthetically, there are indications that the criterion on which our graph is based may comprise all natural waters. ("All natural waters, wherever they happen to be, are closely connected to one another representing a whole " V.I. VERNADSKI, 1933.)

We have already pointed out that our graph anables us to group related water types and that their grouping according to geographical considerations often corresponds to their arrangement in agreement with their geochemical properties. Water metalization, according to MIHOLIC, i.e. its abundance in heavy metals, is in a wider sense, not dependent on other water components or its mineralization. Water metalization is a product of local conditions at the source which render each spring a distinct hydromineral unit.

The here presented data entitle us, in our opinion, to conclude that Cl^- and SO_4^{2-} are the part of water mineralization of a special position. These two anions are conspicuous among the rest by their outstanding contribution to the salinity of the sea water. They are then important component parts of the cyclic salts which the seawater supplies the land through the atmosphere.

Vadose water types, according to CONVAY, contain 95 % Cl^- and about 89 % SO_4^{2-} of cyclic, i. e. marine origin (SAHAMA and RANKAMA, op. cit.) This cannot be said of carbonates, silicates, and other anions, as none are present in rain water.

The water types found in mineral and hot springs are predominatly composed, according to ALLEN and DAY, of vadose water. Even in a region known for its postvolcanic activity, such as Yellowstone National Park, the occurring water is of vadose origin (SAHAMA and RANKAMA, op. cit.) It is obvious then that a considerable part of land waters is under direct or indirect recent influence of the sea water and that they are, by that very fact, influenced by its most important ions, let alone the salt lakes and sources resulting from the dissolving of salt from the still existing layers of the former seas.

The two mentioned anions SO_4^{2-} and Cl^- are of paramount importance on their contribution to the salinity of the hydrosphere. This is the principal reason why our method of differentiation, in our opinion, is natural one, and why favourable results are obtained by it.

The following survey illustrates the properties of the two anions justifying our method.

Properties

of the anion pair Sulfate-Chloride

I. *Common properties :*

1) Quantity : they are the most frequent anions in the Oceans.

2) Mobility : they are the most important anions in the composition of cyclic salts.

II. *Opposite properties :*

CHLORIDES	SULFATES
1/ Their redox potential *is not* altered (1),	1/ their redox potential *is* easily altered,
2/ they are *not* influenced by organisms,	2/ they *are* influenced by organisms,
3/ as *no* insoluble precipitates are formed by them, they *do not* leave aquaeos solutions.	3/ they *are* often precipitated and *leave* aquaeous solutions /in the form of S^{2-}, S^0, SO_4^{2-}/
Chlorides, therefore, are a conservative component in the pair SO_4^{2-}—Cl^-.	Sulfates, therefore, are a dynamic component in the pair SO_4^{2-} —Cl^-.

These two anions seem to be of exceptional importance and value in the composition of any natural water; they seem to have a general character; the ratio of their occurrence must have a deeper meaning than of any other ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, J^-, CO_3^{2-}, $Si\ O_2$ etc.

Here are a few examples to show how usefully our diagrams can be applied :

Owing to its healing properties, the sulphur spring of the Split Baths has been repeatedly studied from the biologic, hydrografic, chemical, etc. points of view by Vouk, Klas, Pax, Vierthaler, Glaser, etc. As far as the content of NaCl is concerned, its water is said to be the richest in Europe (S. Miholic and L. Trauner, 1952).

We have had opportunity to investigate the dynamics, fluctuation, and chemism of this Karst spring in the Adriatic littoral. By applying the above diagram we have found that the water of this spring lies on the " sea line " and that it is an outcome of mixing of about 9/10 of sea water and about 1/10 of a mineral water. This, then, is a water of marine and recent origin (Buljan, 1955).

(1) In conditions prevailing where natural waters occur.

An other exemple: We are indebted to the Soviet geochemist SHISHKINA's investigations for the data ilustrating the chemical composition of the sediment waters in the Black Sea and West Pacific (SHISHKINA 1959 *a*; 1959 *b*). By applying the data to our diagram (graph 4) we find that some of those separated or in way fossile, water types from various depths of sediments undergo changes, (Both Black Sea stations in higher degree, Kuril is station in a lesser degree) and that marine water types sometimes turn into petroleum water types (no changes in water from sediments in stat. 3154!)

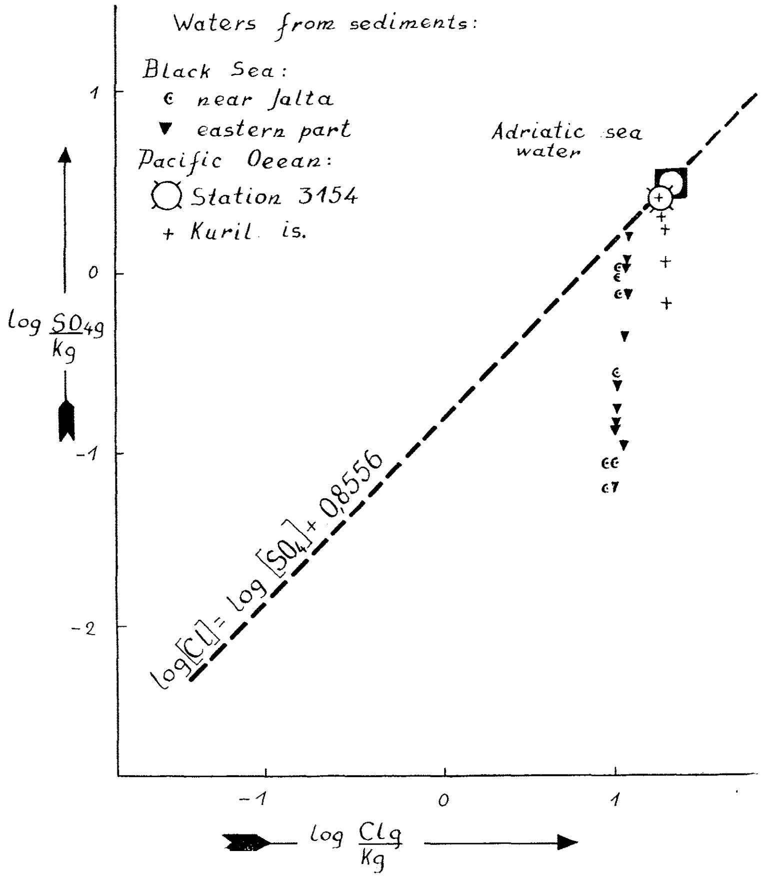

FIG. 4. — *In some places the waters in layers of sea sediments change their chemical composition probably as a result of time of stagnation and of the availability of reducing matter too. E. g. the more deep the layer the lower* SO_4^{2-}/Cl^- *in both stations in Black Sea and in the Sation near Kuril Is* (SHISHKINA's data: 1959 *a* and 1959 *b).*

Our graph seems then to be a useful means in the study of such diagenetic changes of some water types and of their history as well. We do not suppose, however, that our method of determination of natural water types could successfully replace the classification methods now in use, but we hope that, in some cases, it might be of certain help too.

SUMMARY

A number of arguments are offered to prove that the sea water and rain water hold a special place among all the types of natural water.

From that starting-point, and taking into consideration the abundant data referring to chemism of the Yugoslav mineral waters (Miholic), the author has devised his own method of natural classification of waters into their basic geochemical types, basing on the function :

$$\log [Cl^-] = F (\log [SO_4^{2-}])$$

In the course of their circulation on the earth's crust, all the types of natural waters are characterized by Cl^- and SO_4^{2-} ratios and concentrations. This fact has proved very useful, enabling the author to divide all kinds of water into the following types : rain, marine, sulphate, and fossile type. It results that sulphate waters represent the antipodal type of fossile waters. Most of the remaining waters are genetically connected with both the sea water and rain water at the same time.

The enclosed graphs may help us sometimes to explain the history, age, and some other qualities of natural waters. The author has observed and pointed out the circumstance that sulphates and chlorides are particularly important salinity components of svery type of natural water, and that, compared with the other components of water mineralization, they have a more general significance.

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BIBLIOGRAPHIE

1) Bobrov (S.N.), 1959. — Gidrometeoroloskaja harakteristika Kaspiskovo morja. — *Trudy okeanogr. komisiji A.N.SSSR*, Moskva, **5**.

2) Buljan (M.), 1955. — Hydrologic properties and origin of the sulfuric water of the Split Baths. — *Acta Adriatica*, Split, **7** (4).

3) Buljan (M.) et Marinkovic (M.), 1952. — Results of investigations into cyclic salts on the East coast of the Adriatic (Split). — *Acta Adriatica*, Split, **4** (9).

4) Clarke (F.W.), 1924. — The Data of Geochemistry, Washington.

5) Grande (Ch.) et Rodier (J.), 1955. — Contribution à l'étude des eaux thermominérales de Moulay Yacoub. — *C.R. séan. Soc. Sci. nat. phys. du Maroc*, **4**, p. 78.

6) Kalle (K.), 1942. — Der Stoffhaushalt des Meeres. — *Probleme der Kosmischen Physik*, Leipzig, **23**.

7) Klenova (M.V.), 1958. — Geologija morja, Moskva, UCPEDGIZ.

8) Miholic (S.), 1932. — Mineralne vode. — *Priroda*, Zagreb, **22** (6).

9) — 1934. — Kemijsko istrazivanje jodnih voda Jugoslavije Glasnik Hem. — *Drus. Kr. Jug. Kaj.*, **5** Sv. 3. i 4.

10) — 1952 *a*. — Radioactivity of waters issuing from sedimentary rocks. — *Econom. Geology*, **47** (5).

11) MIHOLIC (S.), 1952 *b.* — Kemijski sastav i svojstva mineralnih voda. — *Godisnjak Baln. — klimtl. Inst. NR. Hrvatske*, Zagreb, Sv. 1.

12) — 1957. — The thermal waters of Visegrad in Bosnia. — *A geochemical study. Croatica Chem. Acta*, Zagreb, **20**, p. 39-44.

13) — 1956. — Kemijska analiza termalnog vrela u Fojnici. — *Geol. Vjesnik.*, Zagreb, sv. 8-9, 1954-55.

14) — 1958. — The « Eye water » of Srebrenica in Bosnia. — *A geochemical study. Croatica Chem. Acta*, Zagreb, **30**, p. 29-33.

15) MIHOLIC (S.) et TRAUNER (N.), 1952. — Mineralne vode u Hrvatskoj. — *Godisnjak Balneol. — Klimat. Inst. N.R. Hrvatska*, Zagreb, sv. 1.

16) — 1958. — Die CO_2- Quellen Jugoslaviens Zeitschrift für angewandte Bader-und Klimaheilkunde, Stuttgart, **5** (1).

17) SAHAMA (Th.) et RANKAMA (K.), 1950. — Geochemistry, Chicago.

18) SHISHKINA (O.V.), 1959 *a.* — Himiceskij sastav ilovyh vod Tihovo okeana. — *Trudy Inst. Okeanol. AN. SSSR*, Moskva, **33**, p. 140.

19) — 1959 *b.* — Sulfati v ilovnih vodah Cernovo Morja. — *Trudy Inst. Okeanol. A.N. SSSR*, Moskva, **33**, p. 178.

20) TOLSTOJ (M.P.), 1958. — O podzemnih vodah morskovo proishozdenija. — *Trudy lab. gidrogeol. probl., A.N. SSSR.*, Moskva, **16**.