A CONTRIBUTION TO THE CHARACTERISTIC OF THE HTDROCHEMICAL FACIES OF THE EDGE WATERS OF THE STRATISPHERE

By G. A. MAXIMOVICH

(Communicated by F. P. Savarensky, Member of the Academy, 1.IV.1944)

The waters of the stratisphere are represented by three main types of edge waters: surface waters, artesian epigenetic, and artesian syngenetic waters.

The surface edge waters occur above the surface of erosion. They are common, e. g., in the Mesozoic cover of the Russian platform. Unfortunately, hydrochemical data concerning these waters are very scanty.

Somewhat better studied are the artesian waters of the stratisphere. The investigations carried out during this century have shown that the concentration and chemical composition of waters from the same bed change with depth from its exposures (9, 12, 30, 37, 40, 42). It is therefore possible to speak of hydrochemical facies in connexion with the edge waters of the stratisphere, not only those in the pore spaces, but also such as are confined to a system of communicating fractures, as well as for river waters $(^{29})$.

A hydrochemical facies of edge waters is an area of the water-bearing bed (or a series of beds) distinguished throughout by identical hydrochemical conditions, which may be determined according to the predominance of definite dissolved components (ions, colloids). The concentration and mineral composition of the water of each of these areas varies within a certain range, but the predominance of the same substances persists. Just as in the case of river waters, the hydrochemical facies is determined according to the three components prevailing by weight, and the name given to it is composed of the names of these components in the decreasing order of their value. The change in the chemical composition of river waters as dependent on their concentration has been discussed in a previous note by the same author $(^{29}).$

For the waters of the stratisphere the same regularity holds in its main features (⁴², ⁹, ¹²). To each concentration of edge waters in most cases corresponds a definite composition, a definite facies.

The stratisphere is characterized not only by the same hydrochemical facias as the river, lacustrine and ground waters, but also by some new ones. The occurrence of waters in the pore spaces of the beds, without any communication with the atmosphere above the Earth, in the Earth's crust characterized by peculiar thermodynamic conditions, produces new manifestations of the system: rock \leftrightarrow water \leftrightarrow gas \leftrightarrow living matter, or of the hydrochemical facies.

The hydrochemical facies of edge waters of the stratisphere belong to four formations (groups): the hydrocarbonate, the sulphate, the sodium and the chloride one determined after the first component prevailing by weight. They are listed in the table.

Groups of facies (formations)	Facies
Hydrocarbonate	HCO ₃ -Ca-Na, HCO ₃ -Ca-SO ₄ , HCO ₃ -Ca-Cl, HCO ₃ -Ca-Mg, HCO ₃ -SO ₄ -Ca, HCO ₃ -SO ₄ -C1, HCO ₃ -SO ₄ -Na, HCO ₃ -SO ₄ -Mg,
-	HCO ₃ -Na-Ca, HCO ₃ -Na-SO ₄ , HCO ₃ -Na-Cl(+SO ₄) сульфатная, HCO ₃ -Na-Cl(-SO ₄) бессульфатная, HCO ₃ -Cl-Ca
0.1.1	SO ₄ -HCO ₃ -Na, SO ₄ -HCO ₃ -Ca, SO ₄ -Ca-HCO ₃ , SO ₄ -Ca-Na, SO ₄ -Ca-Cl, SO ₄ -Cl-Ca, SO ₄ -Cl-Mg, SO ₄ -Cl-Na, SO ₄ -HCO ₃ ,

SO₄-Na-Ca, SO₄-Na-Cl, SO₄-Na-Mg, SO₄-Mg-Cl

HCO₃(-SO₄), Na-Cl-SO₄

Cl-Na-Ca(-SO₄), Cl-Na-Mg

Groups

Sulphate

Sodium

Chloride

Main Hydro chemical	Facies of the Edge	Waters of the Stratisphe	ere

The hydrocarbonate facies are characteristic of the slightly concentrated epigenetic waters and are commonly used for water supply purposes. These may be both surface and artesian edge waters.

Na-HCO₃-SO₄, Na-HCO₃-Cl(+SO₄), Na-HCO₃-Cl(-SO₄), Na-SO₄-HCO₃, Na-SO₄-Cl, Na-Cl-HCO₃(+SO₄), Na-Cl-

Cl-HCO₃-SO₄, Cl-HCO₃-Na, Cl-SO₄-Na, Cl-SO₄-Mg, Cl-Na-HCO₃(+SO₄), Cl-Na-HCO₃(-SO₄), Cl-Na-SO₄, Cl-Na-Ca(+SO₄)

The hydrocarbonate-calcium facies are quite common among the Jurassic and Cenomanian water-bearing horizons of the North-Ukrainian trough (³⁰), in the Upper Carboniferous deposits of the Moscow Palaeozoic depression (⁹), in the Paris, Dakota, Wisconsin basins, and in a number of other places.

The hydrocarbonate facies, with increasing distance from the exposure of the bed at the surface or in less permeable, i. e: less mobile areas, with an increase of mineralization are replaced by sulphate facies. This phenomenon has been observed both in the Moscow and in the North-Ukrainian basins.

The presence of unleached sulphates and chlorides within the stratisphere causes the appearance among slightly mobile edge and fissure waters of the sulphate and chloride facies. Thus, the slightly concentrated epigenetic atmogenous waters of the stratisphere change, according to the same general laws as the surface waters.

With growing depth from the exposure of the bed at the surface, a gradual change of facies is observed: HCO₃-Ca- $\mathrm{SO}_4 \rightarrow \mathrm{HCO}_3 - \mathrm{SO}_4 - \mathrm{Ca} \rightarrow \mathrm{SO}_4 - \mathrm{HCO}_3 - \mathrm{Ca} \rightarrow \mathrm{SO}_4 - \mathrm{Ca} - \mathrm{HCO}_3 \rightarrow \mathrm{SO}_4 - \mathrm{Ca} - \mathrm{Na} \rightarrow \mathrm{SO}_4 - \mathrm{Cl} - \mathrm{Na} \rightarrow \mathrm{Cl} - \mathrm{SO}_4 - \mathrm{Na} \rightarrow \mathrm{Cl} - \mathrm{Na} - \mathrm{Ca} - \mathrm{Na} - \mathrm{Na} - \mathrm{Ca} - \mathrm{Na} - \mathrm{Ca} - \mathrm{Na} - \mathrm{Na} - \mathrm{Ca} - \mathrm{Na} - \mathrm{Na}$ $Ca(+SO_4) \rightarrow Cl-Na-Ca(-SO_4).$

This change of hydrochemical facies is traceable in the Moscow basin $\binom{9}{2}$ and at Levshino $\binom{12}{2}$. The local phenomena, as for example, the development of enriched magnesium ores; may sometimes cause the appearance of a specific hydrocarbonste-calcium-magnesium facies. Such are e. g. the waters of the Middle Carboniferous of the Moscow depression (⁹).

The edge waters of the stratisphere are characterized also by new facies which were absent in surface and ground waters. The principal distinction of the waters of the stratisphere is their gas composition $(^{2})$. The underground atmosphere of edge waters is different in composition from the gases of theriv.er, lacustrine and ground waters; a considerable part of which occur above the level of the oxygen surface. It the composition of the underground atmosphere of the edge waters of the stratisphere a predominant part is played by nitrogen, carbon dioxide, hydrocarbons and hydrogen sulphide, in a different facial environment, at different stages of metamorphization of the epigenetic and syngenetic waters and their mixtures. An enrichment in helium permits to determine the age of the waters from the helium to argon ratio $\binom{32}{2}$.

The waters of the pore beds of the stratisphere, changing their place very slowly, are of a higher concentration. A saturation with the most sparingly soluble compounds causes a precipitation in the form of cement of silica, calcium carbonate and calcium sulphate. This is a feature common both to the waters of the stratisphere and to those of lakes.

The anaerobic conditions are the cause of the existence of a peculiar underground biosphere (of the geosphere, and not of the shell ($^{6-8}$, 34 , 35)). In the waters of the stratisphere, under suitable conditions, the processes of desulphation and denitrification are rather extensively developed (1 , 10 , 11 , 13 , 31 , $^{34-39}$). Under the influence of bacterial processes the syngenetic and epigenetic waters of the stratisphere are transformed.

The edge waters of the stratisphere are formed at the expense of two main sources – of syngenetic pelogenic waters $(^{2-4})$ and epigenetic atmogenous waters, as well as potamogenic, thalassogenic and limnogenic ones. According to the geological history of a given area of the Earth's crust, in the bed the syngenetic pelogenic waters are either preserved or gradually replaced by epigenetic waters of a different origin. In different stages of the development of the structure of the Earth's crust different stages of replacement of syngenetic waters by epigenetic ones are observed. These stages of replacement are reflected in a different concentration of the edge waters, in the diversity of the hydrochemical facies.

The edge waters may be monofacial. Such are the syngenetic waters of the Berea sandstone in the Appalachians, represented by the chloride-sodium-calcium facies with no sulphate $(^{43})$. Likewise monofacial are not infrequently the surface waters of the stratisphere, belonging to the hydrocarbonate-calcium facies.

In most cases the edge waters of the stratisphere are polyfacial. Both the epigenetic waters infiltrating to the bed; and the mixture of the epigenetic and syngenetic waters give a comparatively great variety of hydrochemical facies, changing in a regular way with the advance from the exposures of the bed .deeper into the Earth's crust $\binom{9}{12}$.

In addition to a change in the hydrochemical facies in the horizontal direction, they also change along the vertical. The nature of this change depends on the geotectonical setting; geomorphological conditions; development of denudation processes and disjunctive dislocations, and the permeability of the beds.

Under platform conditions the intensity of the movement of the waters diminishes with depth, and along the vertical an increase of the concentration of the solutions is noted, with a corresponding regular change in the hydrochemical facies. This is true of the Palaeozoic waters of the near-Ural; Volga and Emba regions $\binom{24}{2}, \binom{26}{2}, \binom{27}{3}$.

In geoanticline areas, under conditions of a dissected relief, the permeability determines the different relations between the hydrochemical facies. Such is the case both in the Grozny region, and in the Daghestan region, in the Apsheron peninsula, in California, in the Rocky Mountains $(5^{, 14-35}, 33^{, 38}, 40-41)$.

In the Grozny region a decrease is observed in the concentration of the waters from the Sarmatian deposits towards the Karagan and Chokrak deposits; and an increase is noted again in the Maikop deposits. This reflects the preservation of syngenetic waters ($Cl-Na-Ca(-SO_4)$) in the Sarmatian and Maikop and the existence of epigenetic waters and of mixed ones between these two. In the Apsheron peninsula the mineralization diminishes from the Apsheronian and Akchagylian and the upper portion of the productive series towards the lower part of the latter. This corresponds to the replacement of the syngenetic waters by epigenetic and mixed ones. In Daghestan an inverse relation as compared to the Apsheron peninsula is observed in Kai-Kent and Berekey.

The activity of man who exposes the stratisphere by mines and holes results in the appearance of new types of underground waters,, and alters ihe rate of the movement of the edge waters.

By means of wells man unites beds with different hydrochemical facies arid makes appear in the field of develo pm ent of one facies of centres, spots of another one. Such phenomena are of frequent occurrence in oil fields. As a result of oil mining in the Grozny region the abundant hot springs of Goryachevodsk have ceased to exist. The upper horizons of the Grozny region, like those in a number of other oil provinces, that have been made to communicate through a large number of wells, present a mixture of different waters, <of different hydrochemical facies.

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The surface edge waters occur above the surface of erosion. They are common, e. g., in the Mesozoic cover of the Russian platform. Unfortunately, hydrochemical data concerning these waters are very scanty.

Somewhat better studied are the artesian waters of the stratisphere. The investigations carried out during this century have shown that the concentration and chemical composition of waters from the same bed change with depth from its exposures (°, ¹², ³⁰, ³⁷, ⁴⁰, ⁴²). It is therefore possible to speak of hydrochemical facies in connexion with the edge waters of the stratisphere, not only those in the pore spaces, but also such as are confined to a system of communicating fractures, as well as for river waters (²⁹).

A hydrochemical facies of edge waters is an area of the water-bearing bed (or a series of beds) distinguished throughout by identical hydrochemical conditions, which may be determined according to the predominance of definite dissolved components (ions, colloids). The concentration and mineral composition of the water of each of these areas varies within a certain range, but the predominance of the same substances persists. Just as in the case of river waters, the hydrochemical facies is determined according to the three components prevailing by weight, and the name given to it is composed of the names of these components in the decreasing order of their value. The change in the chemical composition of river waters as dependent on their concentration has been discussed in a previous note by the same author (29).

For the waters of the stratisphere the same regularity holds in its main features (⁴², ⁹, ¹²). To each concentration of edge waters in most cases corresponds a definite composition, a definite facies.

The stratisphere is characterized not only by the same hydrochemical facies as the river, lacustrine and ground waters, but also by some new ones. The occurrence of waters in the pore spaces of the beds, without any communication with the atmosphere above the Earth, in the Earth's crust characterized by peculiar thermodynamic conditions, produces new manifestations of the system: rock \leftrightarrow water \leftrightarrow gas \leftrightarrow living matter, or of the hydrochemical facies.

The hydrochemical facies of edge waters of the stratisphere belong to four formations (groups): the hydrocarbonate, the sulphate, the sodium and the chloride one. determined after the first component prevailing by weight. They are listed in the table.

Main Hydrochemical Facies of the Edge Waters of the Stratisphere

Groups of facies (formations)	Facies
Hydrocarbonate .	$\begin{array}{c} \mathrm{HCO_{3}-Ca-Na, \ HCO_{3}-Ca-SO_{4}, \ HCO_{3}-Ca-Cl, \ HCO_{3}-Ca-Mg, \\ \mathrm{HCO_{3}-SO_{4}-Ca, \ HCO_{3}-SO_{4}-Cl, \ HCO_{3}-SO_{4}-Ma, \ HCO_{3}-SO_{4}-Mg, \\ \mathrm{HCO_{3}-Na-Ca, \ HCO_{3}-Na-SO_{4}, \ HCO_{3}-Na-Cl(+SO_{4}) \ sulphate, \\ \mathrm{HCO_{3}-Na-Cl}(-SO_{4}) \ not-sulphate, \ HCO_{3}-Cl-Ca \end{array}$
Sulphate	$\begin{array}{c} \mathrm{SO_4-HCO_3-Na, \ SO_4-HCO_3-Ca, \ SO_4-Ca-HCO_3, \ SO_4-Ca-Na, \\ \mathrm{SO_4-Ca-Cl, \ SO_4-Cl-Na, \ SO_4-Na-HCO_3, \ SO_4-Na-Ca, \ SO_4-Na-Cl-Na, \\ \end{array}}$
Sodium	$\begin{array}{llllllllllllllllllllllllllllllllllll$
Chloride	$\begin{array}{c} \mathrm{Cl-HCO_3-SO_4,\ Cl-HCO_3-Na,\ Cl-SO_4-Na,\ Cl-Na-HCO_3(+SO_4), \\ \mathrm{Cl-Na-HCO_3(-SO_4),\ Cl-Na-SO_4,\ Cl-Na-Ca(+SO_4),\ Cl-Na-Ca(+SO_4),\ Cl-Na-Mg} \end{array}$

The hydrocarbonate facies are characteristic of the slightly concentrated epigenetic waters and are commonly used for water supply purposes. These may be both surface and artesian edge waters.

The hydrocarbonate-calcium facies are quite common among the Jurassic and Cenomanian water-bearing horizons of the North-Ukrainian trough (³⁰), in the Upper Carboniferous deposits of the Moscow Palaeozoic depression (⁹), in the Paris, Dakota, Wisconsin basins, and in a number of other places.

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The presence of unleached sulphates and chlorides within the stratisphere causes the appearance among slightly mobile edge and fissure waters of the sulphate and chloride facies. Thus, the slightly concentrated epigenetic atmogenous waters of the stratisphere change, according to the same general laws as the surface waters.

With growing depth from the exposure of the bed at the surface, a gradual change of facies is observed: $HCO_3 - Ca - SO_4 \rightarrow HCO_3 - SO_4 - Ca \rightarrow SO_4 - Ca - HCO_3 \rightarrow SO_4 - Ca - HCO_3 \rightarrow SO_4 - Ca - HCO_3 \rightarrow SO_4 - Ca - Na \rightarrow SO_4 - Cl - Na \rightarrow Cl - Na - Ca (+SO_4) \rightarrow Cl - Na - Ca(-SO_4).$

This change of hydrochemical facies is traceable in the Moscow basin (*) and at Levshino (12). The local phenomena, as for example, the development of enriched magnesium ores; may sometimes cause the appearance of a specific hydrocarbonate-calcium-magnesium facies. Such are *e. g.* the waters of the Middle Carboniferous of the Moscow depression (*).

The edge waters of the stratisphere are characterized also by new facies which were absent in surface and ground waters. The principal distinction of the waters of the stratisphere is their gas composition $(^2)$. The underground atmosphere of edge waters is different in composition from the gases of the river, lacustrine and ground waters; a considerable part of which occur above the level of the oxygen surface. In the composition of the underground atmosphere of the edge waters of the stratisphere a predominant part is played by nitrogen, carbon dioxide, hydrocarbons and hydrogen sulphide, in a different facial environment, at different stages of metamorphization of the epigenetic and syngenetic waters and their mixtures. An enrichment in helium permits to determine the age of the waters from the helium to argon ratio $(^{32})$.

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calcium sulphate. This is a feature common both to the waters of the stratisphere and to those of lakes.

The anaerobic conditions are the cause of the existence of a peculiar underground biosphere (of the geosphere, and not of the shell $({}^{6-5}, {}^{34}, {}^{35})$). In the waters of the stratisphere, under suitable conditions, the processes of desulphation and denitrification are rather extensively developed $({}^{1}, {}^{10}, {}^{11}, {}^{13}, {}^{34-39})$. Under the influence of bacterial processes the syngenetic and epigenetic waters of the stratisphere are transformed.

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In the Grozny region a decrease is observed in the concentration of the waters from the Sarmatian deposits towards the Karagan and Chokrak deposits; and an increase is noted again in the Maikop deposits. This reflects the preservation of syngenetic waters $(CI-Na-Ca(-SO_4))$ in the Sarmatian and Maikop and the existence of epigenetic waters and of mixed ones between these two. In the Apsheron peninsula the mineralization diminishes from the Apsheronian and Akchagylian and the upper portion of the productive series towards the lower part of the latter. This corresponds to the replacement of the syngenetic waters by epigenetic and mixed ones. In Daghestan an inverse relation as compared to the Apsheron peninsula is observed in Kai-Kent and Berekey.

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