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BASIC PROCESSES AND MECHANISMS OF THE WATER-ROCK SYSTEM EVOLUTION

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A new conception of progressive evolution and self-organizing presence in dead matter is developed; inner mechanisms and processes, realizing this development, are revealed. It is proven that the water-rock system satisfy these requirements.

Introduction

As F.A. Letnikov showed [1], most geological systems belong to dissipative and self-organizing, as they are open, dynamic, consist of numerous components (elements, minerals, rock, atoms), they are developing in nonlinear branch, far from equilibrium. As an example, F.A. Letnikov names minerals growth, clustering, fluid forming, fluid- saline and molten systems, formation of metasomatic, metamorphic and others complexes, et al.

A.S. Scherbakov [2] and others writes about dissipative and self-organizing structures presence in geology. It was shown by us, that the most striking system in geology, able to progressive self-organization is the water – rock system [3, 4].

However, irreversibility and dissipativity of systems in geology, as in physics, was regarded as elements of their degradation, destruction, transition from complex to simple, organization level lowering, et al. Moreover, according to the second law of thermodynamics, it was stated that entropy of the Universe increases steadily and leads to «thermal death» [5]. Though C.R. Darwin proved that biological evolution develops in the opposite to destruction direction: from simple to complex, from lowest to higher forms, i. e. with time system organization level increases, this was admitted as unintelligible exception from common rule.

All talent of I.R. Prigozhin and his follower [6–9, et al.] was necessary to undo this Gordian knot. They started to study the thermodynamics of systems, being far from equilibrium, and determined that such system can reach a certain point (the point of bifurcation) as the result of fluctuation, and after self-organization convert into fundamentally different condition. At the same time, this new condition can be more complicated and from higher order level. To maintain these new (daughter) structures the energy flux from environment is to be higher than it was required for initial (mother) structure, from environment is necessary.

An important point in dissipative systems evolution is that appears a possibility of spontaneous formation of higher-order matters, leading from chaos to order. According to classical science rules – this is impossible, but it happens in nature. According to I.R. Prigozhin, in the stats far from equilibrium, weak disturbance or fluctuation can intensify to giant waves, which destroy one structure and form another, more complicated. Thereby, it was opened by these authors a fundamentally new substantial characteristics of matter, in case of its presence in the conditions of strong deflection of equilibrium.

Hence, irreversible process can be a source not of chaos, but order [5], and nonequilibrium serves as source of order and progressive development. G. Nikolis and I.R. Prigozhin [7] affirm that there is a connection between spatial-temporal structure and functioning of a dissipative system. That is why dissipative systems can possess more complicated organization and more complicated function of development, resulting in complication of interaction mechanisms and evolutionas a whole. Along with complicating of organization, it diversity grows. Thereupon, G. Nikolis, and I.R. Prigozhin [10] write: «we determined that both remoteness from equilibrium and nonlinearity can result in system order. Nontrivial connection appears between order, steadiness and dissipation. To emphasize this connection more distinctly we would name ordered configuration, appearing out of steadiness area of thermodynamic branches as «dissipative structures» [10. P. 71–72].

Concept of dissipative structures of I.R. Prigozhin appeared to be extremely capacious and productive, it became widely spread in many sciences. G. Haken made an important contribution to development of I.R. Prigozhin ideas about these structures forming mechanisms [11], he advanced the conception about cooperative interaction and coherent conduct of definite particles of macro system in the process of their evolutional development. This type self-organization was called by him as synergetic, and science, studying the phenomenon of self-organization he called synergy. Within synergy various problems of physics, chemistry, biology, geography, geology, material science, sociology and others find their solutions. Evolution of the world is represented in the absolutely different aspects, opposite to classical science in many respects. Relatively weak disturbance and fluctuation, which seemed to be unnecessary, appeared to be central in science. The whole content of the evolution changed. If earlier it was regarded as directional process of system change, including cyclic circulation, after works of I.R. Prigozhin they started to be perceived as a process of progressive development, beginnings of more complicated and more organized structures. This type of evolution was called progressive.

The ascertainment of the fact of presence in the Earth's history abiogenous, developing progressively, geological, dissipative structures, existing from the earliest stages of the Earth's history, creates fundamentally new prerequisites of life origin mechanisms' understanding. A new phase exists in dead matter development, which is intervening between nonliving and living matter. During an intervening phase many mechanisms of progressive self-organization were formed, first in the nonliving matter, which further were inherited by biological processes in the more complicated form. Hence, present severance in understanding of dead and living matter evolution mechanisms become not so antagonistic, as it is considered.

At the same time, mechanisms of such a progressive evolution in geological systems, in general, and in the system water-rock, in particular, remain unknown. Moreover, many researches do not admit the fact of progressive evolution existing in abiogenous, geological systems, considering that only presence of biological processes can provide progressive evolution of geological systems [1]. Therefore, examine this question more attentively, conformably to the development of system water-rock in hypergenesis zones.

In hypergenesis areas, as in any other geological system, interaction of water and rock passes in open, equilibrium-nonequilibrium system, where simultaneously equilibrium and imequilibrium exist between individual solid and fluid ingredients. Such system according to V.I. Vernadskiy [12] develops in the conditions of dynamic equilibrium, i.e. in every separate time period inflow and flow-out of matter and energy from every system element, though fluctuate a little, for example according to a year seasons, but in the limit it approaches to some constant.

Water-rock as steady system

Nonequilibrium system is called *steady system when they maintain state permanency in time due to interchange with environment.* Therefore, it is important to examine the peculiarities of steady system water-rock evolution and its connections with environment.

Conformably to investigated system, rock is a constant and unlimited source of chemical elements, which in solid phase are inert, and only by means of water are drawn to active interaction. At that water comes in rock uninterruptedly from external source – atmospheric precipitations, replenishing due to climatic circulation [13]. Rock participates in geological circulation, but in comparison with climatic it is very slow, as it comes to hundreds millions of years. According to M.I. Lvovich [14], climatic circulation of water, in average, in the Earth is accomplished for every 10 days, or 36 times a year (Fig. 1). That is why rock form static part of a system, and water – its dynamic part.

Interacting chemically with rock during filtration, water changes its solution and forms definite geochemical type, which is associated with definite mineral complexes. Hence, relatively to rock, water serves as an element from environment only until hydrogenous mineral complex starts to form.

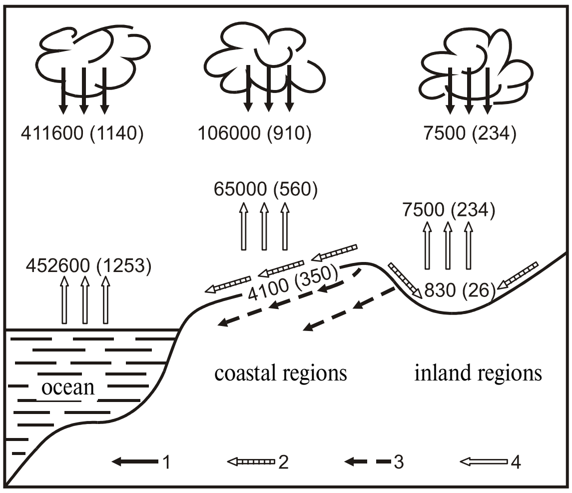

Fig. 1. *The hydrologic cycle. The values given are the corresponding elements of the world water equilibrium: without parenthesis – in km, in parenthesis – in mm (after M.I. Lvovich's data): 1) precipitations; 2) surface runoff; 3) underground runoff; 4) evaporation.*

In essence, the water-rock system as steady appears from the beginning of these system-forming elements interaction. As hydrogenous mineral complex starts forming practically from the moment of interaction, these processes approximately coincide in time. It is evident from mentioned above, that water, as exterior component relatively to rock, becomes an inner part of a system from the beginning of interaction and secondary product forming.

Thus, nonordinariness of steady water – rock system consists in that one its element (rock) is fixed, stable, solid element, i.e. possesses characteristics of conservative system. At the same time, rock possesses can pass through itself water, possessing dissipative structures characteristics, which during development result in irreversible process [7]. The second element (water) is a moving element, which runs through the first, straining with its help.

The second nonordinary peculiarity of the examined steady system is that one of the elements (water) plays a role of external and simultaneously internal component of this system. Water, on the one hand, being an element of circulation, provides system connection with environment, and on the other hand, being an element of the system, provides development and secondary product forming.

If we add to the mentioned above that the water-rock system is of equilibrium-nonequilibrium state from the chemical point of view [15], i. e. water is able to interact continuously for a geological long time with rock, forming new hydrogenous-mineral complexes, it becomes evident that the system under review is absolutely unique from physical and chemical point of view.

An important feature of steady system is constant matter and power receiving from environment. This aspect of a problem also has peculiarities. Let's start from the most important matter – water.

Though, atmospheric precipitations come in rock discretely, it does not prevent constant interaction of water with rock. Interaction permanency is provided by the fact, that rock, due to low permeability are not able to let all the volume of precipitations pass, the most part of them constantly flow down to seas in the form of surface runoff. Surplus water provides full fillup of rock interstices. Only in the zone of aeration, a part of interstices, in some period of the year, can be filled not entirely with water. All these guarantee continuity and permanency of water and rock interaction.

Now we will regard the state stability of the system under review. It is well known, that groundwater suffer changes during the seasons, different years, longstanding cycles, et al [16]. But can such changes break the stability of steady water – rock system action. This question was examined by us in details [17]. With this purpose, we have analyzed time and space changes in groundwater composition of basic hydrogeological provinces of the globe and proved *the waters of each province possess specific, different from other provinces composition, which preserve its individuality during all time and spatial changes.* Particularly, it was shown that temporal variations of groundwater parameters of hypergenesis zone, undoubtedly, occur, they change continuously in various manner; but these changes occur fluently and apply to all components without exclusion, which are connected somehow. Though, variations of each of components changes differently, but in such a way, that connections between them remain unbroken and go beyond the scope of values, which are peculiar for waters of given geochemical types. All changes are limited in freedom degree and do not result in individuality obliteration of every geochemical type, character for one or another hydrogeological province.

From the analyses of seasonal variation scale of water solution in different provinces, the following conclusions were made:

1) Temporal variations in the composition of water in any landscape zone, as a rule, do not cause a change of the basic features, characterizing its geochemical type;
2) The geochemical type of groundwater is not fully controlled by the regime of its recharge but is related to its numerous fundamental connections with all landscape components. Changes in supply pattern in different year season – is only one of these parameters, which are not able to break the connection;
3) The parameters of each geochemical water type in various hydrogeological provinces, in aggregate, are quite stable and individual, though each can be blocked by other water type in some year periods.

We consider also the problem of spatial variations in groundwater composition along the infiltration flow path from recharge to discharge zone. It was determined that groundwater composition in all landscape areas and provinces is changing along the infiltration flow. Though, these changes are not significant to transform one geochemical type to another. This implies that *geochemical specificity of groundwater is already formed in recharge zone and is increasing constantly along infiltration flow.* The most important indicator of such specificity is general TDS, pH, O_2, CO_2, SiO_2, Fe, Al, K, P and S content, chemical water type, ratio between separate elements, et al.

All these allow us to draw several conclusions:

1) The geochemical set of elements in water solution of hypergenesis zone form quite stable system, whose temporal and spatial changes do not affect basic parameters;
2) In every landscape type and hydrogeological province, an individual, stable hydrogeochemical system is formed, it provides the variation possibility of separate parameters, but only in strictly determined limits;
3) The individuality and stability of hydrogeological system is provided mainly by water cycle character, small distance between recharge and discharge zones, presence of complex connections with environmental components;

The given conclusions were published by us in 1988 [17]. Later, when preparing the 3d edition of V.I. Vernadskiy's book «History of natural waters», we have found his absolutely unique understandings regarding this problem.

It appeared that «empiric thesis about *permanency of natural water chemical composition within definite variations of their composition* (emphasized by us – S. Sh) came into scientific perception in the end of XIX – beginning of XX century», but it was never «expressed in definite and clear form and it was not process and examined critically», though in reality it is the cornerstone of our knowledge and a basis the current scientific research. The necessary conclusions were not made from it yet» [12, P. 256].

One cannot, but wonder the astuteness and ability of this great scientist to understand that, which was not stated «in definite and clear form» of this great scientist. Unfortunately, this thesis did not appear in science even in present times, though it was 75 years ago when these lines were written. This is how a great scientist formulates this empiric thesis: *«the chemical composition of every natural waters can be expressed for each chemical element in limit minimum and maximum values, which are not displaced in short period of historical time. An average of chemical composition, derived from this, is a constant value in historical time* (*emphasized by the author* – V.V.) [12]. This average can be maintained for a given water during geological time also». Consider this expression can be called V.I. Vernadskiy postulate about water composition permanency.

After this conclusion of V.I. Vernadskiy, it is hardly doubtful that steady water-rock system can function geologically for a long time in stable state.

Hence, from the moment on water beginnings on the Earth, steady equilibrium-nonequilibrium water-rock system appeared, it possesses self-contradictory character, determining it ability to spontaneous, continuous, geologically long termed development, along with forming fundamentally new mineral phases and geochemical water types. This system, within the earth crust, develops constantly in nonlinear region of thermodynamic branch, in conditions, far from equilibrium; it relates to abiogenous dissipative type, which plays a special role in progressive development of dead matter [4]. An important peculiarity of this system consists in the fact, that one component (water) is exterior and simultaneously interior element, what along with equilibrium-nonequilibrium state and presence of various phase components provides an internally contradictory state and progressive development. This is only one example.

Mechanisms of changing one secondary mineral by another

As it was shown by us [17], on the earliest stages of water interaction with alumina silicates, hydroxides Al – gibbsite, boehmite, diaspore, baierite, et al. are forming; they connect practically all Al, coming in the solution from endogenous alumina silicates. At the same time, Si content, not connected with hydroxides, is growing in solution as water and aluminum silicate interaction time increases. Such a growth of Si content results in kaolinization of the solution by kaolinite according to the following reaction:

$$2Al^{3+}+6OH^{-}+2H_4SiO_4=Al_2Si_2O_5(OH)_4+5H_2O, \quad (1)$$

Its constant is

$$K=1/[Al^{3+}]^2[OH^-]^6[H_4SiO_4]^2 \quad (2)$$

equal to $10^{79,4}$. From this moment kaolinite starts to form. But what happen with gibbsite? Does it continue to form?

To answer these questions, one needs to compare the kaolinite composition with the composition of initial minerals, soluble by water. Initial igneous rock, in average, contains Si in 3,7 times more than Al. Kaoliniteite contains Al and Si at the same value in atom and weight content. Hence, during kaolinite forming, Al, not Si, is a critical element, i.e. kaolinite formation scale are determined by the scale or quantity of Al, not Si, coming in the solution, as the quantity of Si is superfluous. Kaolinite, during its formation, connects all Al, coming in the solution, as the solution is saturated earlier, but not all, only a part of Si, necessary to built kaolinite lattice. But if it is so, Al does not already suffice to form gibbsite; hence, it cannot be formed. Considering the unique importance of the discussed mechanisms, examine it more accurately.

So, ultra fresh precipitations, coming in magmatic rock dissolve all minerals, from which it consists. Though, dilution kinetics of the various minerals is different [15, 18], during the first period of interaction, all chemical elements turn to solution, approximately in the same correlation, which exists in rock. In any case, Si turns in the solution in the greater amount, than Al; but as it is already shown, groundwater according to equilibrium constant firstly became saturated with gibbsite, and then with kaolinite (Fig. 2)

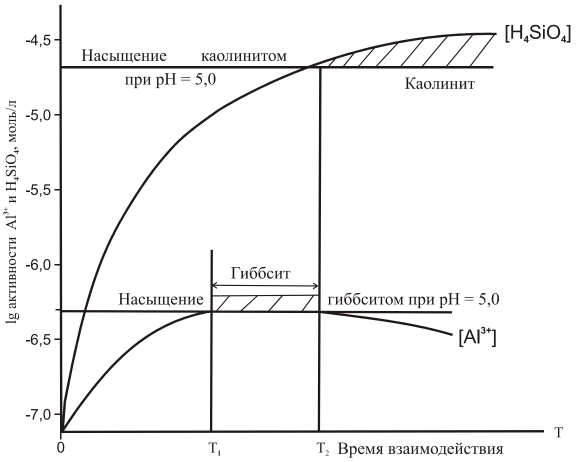

Fig. 2. *Schematic diagram showing the dependence of the formation of gibbsite and kaolinite on the time of groundwater and endogenous alumina silicates interaction.*

Explanation to Fig. 2: Насыщение каолинитном – saturation by kaolinite; каолинит – kaolinite; насыщение гиббситом – saturation by gibbsite; гиббсит – gibbsite; время взаимодействия – interaction time

With pH 5 water solution saturation with gibbsite, according to reaction (3) and constant (4)

$$Al^{3+}+3OH^-=Al(OH)_3, \quad (3)$$

$$K=1/[\,Al^{3+}]\cdot[OH^-]^3=10^{33,2} \quad (4)$$

occurs at Al^{3+} activity equal to $10^{-6,2}$. Such an activity value is reached relatively quickly, time of interaction is equal to T_1 (Fig. 2). From this moment starts gibbsite load. But, as interaction water continues to interact with endogenous rock, opposite to aluminum, silicon continues to concentrate in the solution that eventually results to equilibrium with kaolinite according to reaction (1). Such a equilibrium, in pH 5,0 starts in H_4SiO_4 activity, equal to$10^{-4,7}$.

Hence, kaolinite is formed after gibbsite, i. e. as a result of longer water and endogenous minerals interaction, which we mark as T_2 (Fig. 2). But kaolinite forming, as it is shown above, does not connect all silicon, turning to solution, which due to this continues to concentrate in the solution. But if it is true, than according to constant (2) with one and the same pH value, Al^{3+} activity not only can not increase, but should decrease, this breaks the equilibrium with gibbsite, which cannot form in this conditions and is replaced by kaolinite.

From mentioned above it is clear, that *gibbsite and kaolinite are competitive minerals: they are «fighting» for a right to possess Al, coming in the solution from endogenous rock.* At the first stage gibbsite manage to do this, at the second – kaolinite succeeds; it represses the possibility of gibbsite forming. That is why bauxites do not from at the other stages of water and rock interaction, but for the first.

Thus, from the first moments of interaction between water without chemical elements and endogenous alumina silicates when $T_x < T_1$, no secondary element appear. When $T_1 > T_x < T_2$ gibbsite forms, when $T_x < T_1$ – kaolinite forms, all other minerals are formed subsequently in accordance with Fig. 3. Of course, natural process is more complicated, as pH changes – usually it is increasing, therefore gibbsite is not formed and dissolved when $T_x > T_2$. In any case, it is important, that in nonliving water-rock system there is mechanisms, controlling and directing evolutionary path of such interaction. It is more important to emphasize that *the process of water-rock system interaction always develops in one direction: along the line from point A to point I* (Fig. 3). Explain this thesis: if water, containing a deal of elements is in equilibrium, for example, in the point E, so coming in the rock, it starts to interact with it in such a way, that it would form but not dissolve calcite and, accumulating elements, would aim forward in the direction of F point and, in no circumstances, to point D (Fig. 3).

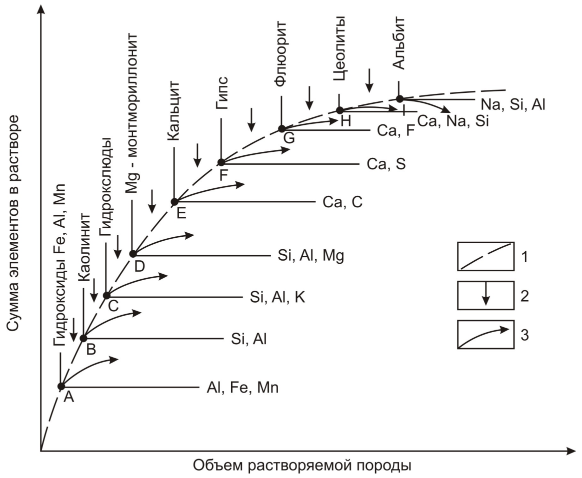

Fig. 3. *Generalized diagram showing the relations of dispersed and accumulated elements during the evolution of water-rock system. A-I, points corresponding to the beginning of formation of a new secondary phase. 1) curve of accumulation of dispersed elements. 2) zones of possible water input to the contact with rock, and 3) sites of possible cessation of water-rock interaction.*

Explanation to Fig. 3.: Сумма элементов в растворе – the sum of elements in the solution; гидроксиды – hydroxides; каолинит – kaoliniteite; гидрослюды – hydromicas; монтмориллонит – montmorillonite; кальцит – calcite; гипс – gypsum; флюорит – fluorite; цеолиты – zeolites; альбит – albite

The very existing of mechanisms of competition of unilateral character evolution between minerals in nonliving nature is very interesting and important. This is one more argument for self-organization process existing in dead matter, which we consequently reveal in the system water-rock [3, 19] and which is the object of research. But continue to examine secondary minerals' forming mechanisms.

By the example of gibbsite and kaolinite we demonstrated that *different from soluble rock correlation of chemical elements in the newly formed minerals is an important mechanisms of deep differentiation (redistribution) of chemical elements in water solution; this is a basic reason for change paragenic associations of forming secondary elements in evolutional development of the water-rock system*. At the same time, various mechanisms influence is possible. Let's give another example.

The quantity of forming calcite in the water-rock system is determined by the scale of Ca transition in the solution, not taking into consideration water, carrying away out of the system. This is true, if there are no competitive minerals. At the earlier stages Ca-montmorillonite performs this function for calcite, it's conditional constant is significantly lesser than calcite. Superfluous Si, accumulating in the solution, gradually results in equilibrium with Ca-montmorillonite, which, at a definite stage of interaction of the water- alumina silicates, forms according to the reaction (5)

$$0{,}167Ca^{2+}+2{,}33Al^{3+}+3{,}67H_4SiO_4+7{,}32OH^-=$$
$$=Ca_{0{,}167}Al_{2{,}33}Si_{3{,}67}O_{10}(OH)_2 \qquad (5)$$

its constant is (6)

$$K=1/[Ca^{2+}]^{0{,}167}[Al^{3+}]^{2{,}33}\cdot[H_4SiO_4]^{3{,}67}[OH^-]^{7{,}32} \qquad (6)$$

equal to$10^{89{,}3}$. When pH 7,5, activity Al^{3+} $10^{-7{,}2}$ and Ca^{2+} 10^{-3} groundwater saturation with Ca-montmorillonite is already taking place at activity $H_4SiO_4 > 10^{-6{,}6}$. But forming mineral connects Ca in a small amount: Si/Ca correlation in montmorillonite amount 22, and clarke correlation in the igneous rock is about 10 (more for granites). From this follows, that Ca-montmorillonite is not able to connect all Ca in the formation process, which therefore continues to accumulate in the solution and serves as a source for calcite forming.

The given example proves that though Ca-montmorillonite is a competitor for calcite, this competition is not severe, as between kaolinite and gibbsite, and it does not prevent late calcite forming. The last cannot «forbid» Ca-montmorillonite forming, as H_4SiO_4 always accumulates in the solution, it's growth provides this compound forming earlier or later. That is why these minerals coexist frequently, and this provides forming of such unique formation as loess.

Continuing calcium minerals examination of later stages (gypsum, fluorite, apatite, et al.), it is evident that calcite, connecting Ca, is a competitive for them, but not severe, as it do not forbid their forming. In this case, that mineral profited, which anionic part (CO_3^-, PO_4^{3-}, SO_4^{2-}, F^-) presents in the greater amount in the mineral forming environment, i.e. anion competition starts. All these diversify mineral complex.

In the given research, we do not pose a problem to examine all elements and minerals behavior. We want to reveal only the mechanisms, which result in the change of paragenic of secondary mineral complexes and lead to diversification of forming, secondary, mineral products. Therefore, it is evident that *one and the same rock, soluble by water, forms various secondary minerals in different interaction stages.*

It is evident from the mentioned above, that succession of secondary minerals forming is determined by many factors, which are amenable to quantitative evaluation, relatively to concrete conditions of geological situation. It is always possible to estimate theoretically such succession, but one needs to know the parameters of water solution and direction of its change. Finally, it is water composition which determines the character and stages of secondary mineral formation.

Ascertained mechanisms of evolution of the water-rock system, as it was already shown, are fundamental and acts independently from exterior factors. At the same time, the water-rock system is an open and steady one, as it exchange matter and power with an environment, which controls temperature, pressure, correlation of water and rock masses, water filtration speed, initial water composition, type of soluble rock, their mineral composition, time of internation; water movement way, et al. so it is important to reveal the exterior factors role, influencing the development of the water-rock system.

The main question, appearing at the same time, is why within limits of one and the same rock (granites, basalts, et al.) do various secondary products form? Not only are numerous scientists looking for an answer to this question, but entire sciences: soil science, landscape sciences, groundwater hydrology, geochemistry, mineralogy, sedimentology, physical geography, crusts weathering, minerals sciences, et al. The most typical answer is the temperature changes, precipitations quantity, evaporation, biological productivity, relief, et al., but all these do not make mechanisms of this or that factors action clear.

It is evident that simple enumeration even of a hundred factors does not solve the problem. Another method is necessary, based on the fact of equilibrium-nonequilibrium condition of the system water- alumina silicates. In particular from the proved fact of groundwater nonequilibrium with endogenous alumina silicates and their interaction continuity [15] result to an important principle: *the longer interaction, the greater amount of chemical elements appears in the solution.*

Hence, the most important from exterior factors is *time of water alumina silicates interaction* which dissolve by water. It is surprising, but just this factor is usually forgotten in enumeration of many others. Even if it is mentioned, mechanism of its action remains undisclosed. Considering current situation, examine this question more elaborately.

The natural water – endogenous alumina silicates system is nonequilibrium in various parts of geological section, that determines though slow, but continuous transfer of chemical elements in water solution, which was proved by numerous laboratory experiments. At the same time, irrespective of dissolve mechanism (conguous or incongruous), reaction finishes by complete dissolution of primary minerals and precipitatation of secondary ones. That is why the boundaries between primary and secondary minerals are strict [15, 18, 20–22].

For example, the generalized reaction of albite transformation to sanidine and verse (7)

$$NaAlSi_3O_8+K^+ \Leftrightarrow KAlSi_3O_8+Na^+, \qquad (7)$$

according to experimental researches data is realized in two stages 1) congruous sanidine dissolution (8) and 2) albite precipitation (9) [18]

$$KAlSi_3O_8+8H_2O=K^++Al(OH)_4^-+3H_4SiO_4^0, \qquad (8)$$

$$Na^++Al(OH)_4^-+3H_4SiO_4^0=NaAlSi_3O_8+8H_2O, \qquad (9)$$

As D.R. O'Neill and X.P. Taylor mentioned, transformed part of a crystal should «cross the solution river» to become another mineral [20]. With increasing of interaction time, concentration of chemical elements in the solution firstly increases rapidly, than increases slower. The same process happens with increasing of interaction surface [18]. It is important, that chemical interaction develops geologically long time. Even when secondary products cover the surface of dissolve endogenous mineral, chemical interaction continues, as secondary minerals from porous layer, impedimental further endogenous aluminum silicate dissolution.

It is possible to evaluate a time of interaction of water-rock according to groundwater runoff value, which is basic parameter of more general concept – water exchange. Water exchange, as a function of precipitations quantity, their evaporation degree (temperature), relief ruggedness and rock permeability, determine values and speed of water movement in concrete geological structure, and consequently, time of water and rock interaction, playing the most important role in this system. Hence, water exchange is an integral factor of interaction time in the water-rock system: the more is water exchange, the less is interaction time and verse versa. That is why the water exchange notion is a basic in understanding of mechanisms and scales of water and aluminum silicates interaction [17]. We move to examining of this question.

Water exchange as the most important factor in hydrogenous-mineral complexes forming

Thus, as a time parameter of water and rock interaction, it is more suitable to use water exchange data. To specify preliminarily, we would understand under this, in particular, whether the groundwater runoff modulus is a water exchange measure.

First of all, modulus runoff – is water quantity, runoffing per time unit from area unite. Groundwater runoff modulus is the similar, but for groundwater. The most frequently used unit is $l/s{\cdot}km^2$.

Such a method, developed by hydrologists is more or less authentic, concerning surface runoff, though even in this case it is hard to imagine the water to flow only on the daylight, and completely left untouched the volume of rock, soils, zones of suspended water, et al.

The situation changes dramatically, when we speak about groundwater runoff. It is evident that in this case water runoffs not on the rock surface, but strains through rock volume, but even in this case hydrogeologists and hydrologists speak about groundwater runoff modulus and express it in the same unites.

It is evident from the definition that runoff modulus M is equal to

$$M=Q/F, \qquad (10)$$

where Q is the water quantity, flowing from some area per time unite, for example, m^3/s, F is the territory space, m^2. In this case modulus unit of runoff is m/s, i. e. physically it is water movement speed unit.

Admitting that water flows not from relief surface, but move through some rock, than Q should be divided not on F, but on V is rock volume, m^3. In this case

$$Q/V=1/T=WE, \qquad (11)$$

where T is the time of water presence in rock, and WE is water exchange index.

Hence*, water exchange – a value, reversed to time, during which water is located in rock and interact with it.* The longer this interaction – the less is water exchange and verse versa (12).

According to equations (10) and (11) it is evident that

$$WE= M/h, \qquad (12)$$

where h is the power of zone, through which water is filtered, or in other words, the power of active water exchange zone. Of course, one should remember that water exchange is the same along not all filtration area: as a rule it decreases with a depth. Moreover, there are always areas of high and low permeability; this reasons the difference of water exchange on various depths. Hence, it is possible to speak about some average values, conformably to some area of groundwater movement, understanding, that real situation is more complicated.

After determining the water exchange notion, now turn to the role of this factor in the evolutional development of the water-rock system and in forming hydrogenous-mineral complexes.

First of all, it is necessary to mention that water exchange role in forming of all hypergenesis zone products (soils, crusts, erosion, landscapes, natural waters, et al.) is not just unrevealed, but this factor is mentioned very seldom among many others. Instead of water exchange, atmospheric precipitation are used, the quantity of which is usually associated with water exchange: the more precipitations are, the higher is water exchange and verse versa. Though this connection was not proved by anybody, and of course it is not linear, as water exchange is not just precipitation derivative, but derivative from evaporation, permeability of rock, relief, et al., it still was used by many scientists.

In the earliest researches, we characterized water exchange intensity through modulus of groundwater runoff. Analysis of numerous factual data made us conclude that «to each water exchange type is peculiar to a set of secondary mineral phases and geochemical water types» [17]. This dependence later will be proved by us with new data.

Generalizing all data on hypergenesis zone of the earth, we succeeded in determination of approximate time of interaction of water with rocks in various landscape zones (table). In spite of the fact, that these data are approximate, they create an impressive picture. Time of water-rock interaction or water age in various climatic zones vary from tens to millions of years. The received numbers accuracy is proved by data on absolute water age.

As it was already mentioned, age of the deepest soda waters of Oklahoma (USA) reaches 40 thousands of years, i.e. it is close to values presented in the table. It should be considered that examined water did not output the aquifer and interaction with rock continues. The second example can be given according to north Italy territory, Lomellina basin, located within Po plain. The depth of examined head water reaches 230 m. Fresh water with 0,2...0,4 g/l salinity, their age is 5...7 sometimes 18 thousand of years [23].

Table. *Approximate time of water-rock interaction for various hydrogenous-mineral complexes*

Complexes	Subsurface runoff, l/(s·km^2)	Flow area power, m	Time of interaction, years	Water exchange, years^{-1}
Laterite	30,0	15	16,7	$6 \cdot 10^{-2}$
Kaolinite	8,0	30	125	$8 \cdot 10^{-3}$
Bisiallite	2,0	150	2500	$4 \cdot 10^{-4}$
Soda-loess	0,3	300	$32 \cdot 10^{3}$	$3 \cdot 10^{-5}$
Gypsum-forming	0,08	300	$12 \cdot 10^{4}$	$8 \cdot 10^{-6}$
Halite-forming	0,01	400	$14 \cdot 10^{5}$	$7 \cdot 10^{-7}$
Organogenic	0,15	10	2000	$5 \cdot 10^{-4}$

One more example is aquifer of Bassis-Laurenties territory, Quebec province, Canada. Here in sediment rock of quaternary age fresh water is developed, they are examined till 140m depth. The age of such water constitutes several thousand years, sometimes Cl-Na waters can be found with mineralization up to 10g/l, which according to research authors are expressed from sea clay and mixed up with fresh water. The age of such water reaches 12 thousand years [24].

The given examples, including Canadian sheet data [25, 26], which can be continued, proved that, received by us, order of values of time interaction coincides with water age in the published data. Unfortunately, there is no information, concerning the absolute age of salty water, forming salt. That is why, the age of halite-forming complexes is less determined.

The data received unambiguously proves that *every hydrogenous-mineral complex forms in various water exchange types. At the same time, there exist strict and complicated dependence between complex composition, water exchange intensity and water salinity** (Fig. 4, *a*). The laterite complex is formed at the most active water exchange, halite-forming – at the weakest water exchange. All the rest occupy intermediate position. Water exchange values can change for thousands of times, and these are according to average readings. If one takes extreme value, the difference would be in millions of times.

An important meaning is the organogenic complex point position, which shifted sharply to the left, i. e. to the side of less mineralization of water from composite curve (Fig. 4, a). this means, the during one and the same interaction time, the total groundwater mineralization is significantly less in marsh environment, than during interaction of the same water volume with rock, i. e. daughter subsystem of water an organic matter, provides the solution with salts in less degree, then mother subsystem – waterous rock.

It should be also emphasized that hydrogenous-mineral complexes dependence from subsurface runoff

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* It should be mentioned, that the picture is made in the logarithmic scale.

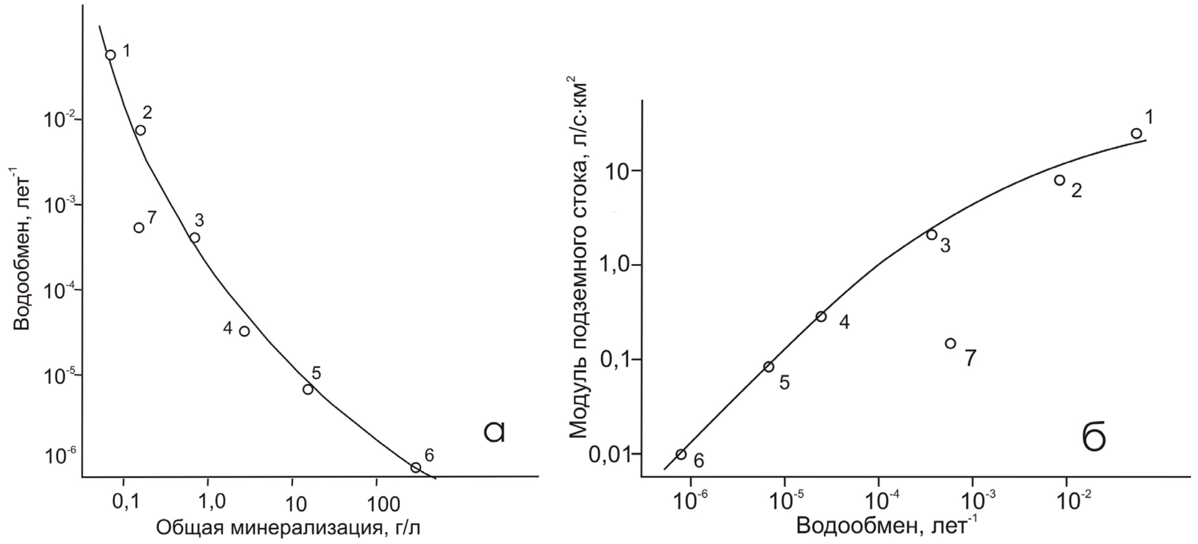

Fig. 4. *Hydrogenous-mineral complexes. Dependence of the composition from water and a) water salinity; b) modules of subsurface runoff. 1) Laterite; 2) Kaolinite; 3) Bisiallite; 4) Soda-loess; 5) Gypsum -forming; 6) Halite-forming; 7) Organogenic*
Explanation to Fig. 4.: Водообменб лет – water exchange, years; модуль подземного стока – module of subsurface runoff; общая минерализация, г.л – total dissolved solids, g/l

modulus (Fig. 4, a) and water exchange intensity (Fig. 4, b) differ greatly. If in the picture 4, a we observe linear dependence between flow modulus and hydrogenous-mineral complexes location, in the picture 4, b this dependence from water exchange intensity within similar logarithmic scale of data becomes parabolic, i.e. more complicated.

Thus, *variations in water exchange, even within the same climatic zone and the same rock type, result in forming of hydrogenous-mineral complexes.* During active water exchange (interaction time of the first decades), the water-rock system, as an automatic machine forms only laterite complex. This process continues until and only on those areas, when and where such water exchange occurs. With water exchange decreasing in the same climatic zone, within the same rock types with interaction time increasing up to hundreds years, the water-rock system transforms into new quality and forms Kaolinite complex. Areas of relatively slowed water exchange in tropics are character for river valleys, where deeper runoff is unloaded. That is why in watershed areas laterites are usually developed, and in the river valleys – kaolinite complex. Earlier this was explained from the position that laterites are remains of ancient peneplains and that kaolinites are located below, but his opinion turned out to be wrong.

Weathering products distribution on the space and depth depending on water exchange is peculiar not only for laterite hydrogenous-mineral complexes, but for all the rest, including soda-loess and organogenic. But laterite complex example is more demonstrative and many scientists paid attention on this.

Conclusion

Due to equilibrium-nonequilibrium state, the water-rock system is able to interact for a log geologic time everywhere, where there are water and aluminum silicates, with which it is nonequilibrium and dissolve them. At the same time even the most fresh water with mineralization <0,1 g/l is already equilibrium with Al hydroxides, which it forms. With water salinity increase, the character of equilibrium changes, and a system products numerous secondary minerals, equilibrium with water solution. Severe paragenic connection between secondary mineral products and water composition occurs from this.

Water salinity is function of water and endogenous alumina silicates interaction time. Unfortunately, this function is not of linear character, but more complicated one, it is reasoned by consecutive deposition from the solution of various minerals of different chemical composition, by mixing genetic water types, et al.

Water-rock interaction time, though is continues, but differs greatly according to duration, not only in different climatic zones, but in different depths of interaction. Water, percolating at various depths of geologic section, acquires different filtration speeds and consequently interaction time.

Using water exchange and equilibrium state as basic parameters of the water-rock system evolution, we managed to determine that at the different water exchange, different secondary minerals are formed and consequently groundwater geochemical types. Speaking in other words, *water interaction with alumina silicates is different at different water exchange and results in forming of different solid and solute secondary products, the accumulation of which we call hydrogenous-mineral complex.* At the same water exchange, the water-rock system, as an automatic machine forms one and the same secondary hydrogenous-mineral complex (laterites, clays, loesses, salts, et al.) during geologically long period of time, with corresponding water type, geochemical medium character, et al.

During water exchange change, one hydrogenous-mineral complex is replaced by another. For example, very often laterite type of weathering is replaced by Kaolinite, or soda waters are replaced by saltish SO_4-Na, Cl-SO_4-Na, et al. All these makes the situation more complicated, forms a contrast environment, various types of geochemical barriers, secondary mineral, et al. Water exchange *character change is a basic mechanism of the observed replace of latitude, waist and vertical zoning, in the hypergenesis zone.*

The character of water and primary alumina silicates interaction changes depending on the duration of water-rock contact: on various stages, the system forms various hydrogenous-mineral complexes. It is important to emphasize that the development of the research system always occurs in one direction.

Hence, geological development of the water-alumina silicates system in the condition of a certain water exchange results in forming of a steady, geochemical medium, being that base, to which strictly determined forms of living are accommodated. They are different in various environments, including spices, forms, morphology, bioproductivity, and biogeocenosis in general. Moreover, water exchange determines the type of organic matter decomposition. All these in common create not only geochemical, but biogeochemical environment, hence numerous geological and biogenic processes and phenomena.

The water-rock system, according to characteristics, peculiarities and processes complex, forms abiogenic, dissipative progressively self-organizing structure, which originated at the earliest stage of the Earth development at the time of free water appearance. This system ability to progressive self-organization determines it as the fundamental and basic unit in the inorganic matter development at the prebiotic stage of dissipative structures evolution. Exactly from this system numerous others systems appeared, inherited many characteristics from it. Formed as a result of this system evolutional development, secondary hydrogenous-mineral complexes, multiplying, gradually occupied the geological space, new lithosphere strata, formed new geochemical medium, which determined the new miner phases forming, influencing the environment character. This process is geologically endless. This is the sense of self-organization in mineral system, including origin, growth and time-spatial distribution of new structural forms, mineral constitutions, and geochemical environments.

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