

Water-Rock Interaction: Implications for the Origin and Program of Global Evolution

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Abstract: Evolution was thought for several hundreds of years to be restricted to biological systems and to have originated together with life. This idea remains quite broadly supported at present though recent research in synergetics shows that any open system existing far from equilibrium can evolve and reach more complicated states. Such an open system exists in geology: it is the water-rock system having particular basic properties. It is a nonlinear equilibrium-nonequilibrium system, which receives solar energy and undergoes intrinsically driven evolution, at any external conditions, to produce ever new secondary minerals and chemical types of water. Thus, the water-rock system is suggested to have been at the origin of global evolution.

Keywords: Composition of water, equilibrium, hydrogeochemistry, internal evolution, water-rock interaction, mechanism of evolution, program of global evolution

Introduction

Evolution is often called “the greatest show on earth” for its universality, global scale, and uniqueness. Its mechanisms are still an enigma though being discussed in great many books and papers for more than a hundred of years. Darwin’s idea of natural selection has well taken roots in the minds of scientists but it fails to give exhaustive explanations for the onset, mechanisms, and intrinsic motives of the global evolution. As Richard Dawkins (2009), famous biologist, admits, the beginning of evolution remains vague in spite of all advances in biology.

Evolution was thought for a long time to be restricted to biological systems but the today’s synergetics has broaden the concept by showing that all dissipative systems can evolve irreversibly under certain conditions. The state of a system far from the equilibrium is one such condition. Nonequilibrium systems fluctuate continuously, can arrive at bifurcation, break down, and proceed to a more complex state as a result of self-organization. This more complex state may have a higher organization level if the system receives energy from the exterior (Prigogine, Stengers, 1984). Synergetics, however, either, cannot explain the very onset and mechanisms of evolution.

There are two points that may preclude clear understanding of the global evolution. First, scientists, since Charles Darwin and Alfred Wallace, have overlooked water in their search for the evolution mechanisms. The investigation into such a fascinating show as the evolution has had no place for water known

to be critical for life. A half of all water is stored in the biosphere: it makes at least 60-65 vol.% in any organism or even sometimes up to 98%, as in medusa, and about 70% in a human body. Water, like blood vessels, penetrates through the biosphere and the lithosphere.

According to Vladimir Vernadsky, whose 150th anniversary we celebrate in 2013, - water is the most particular substance on our home planet, which controls both biological and geological systems. It drives the life of individual organisms and the biosphere, as well as the abiotic processes of weathering, sedimentation, diagenesis, catagenesis, metamorphism, magmatism, metallogeny, etc. The interaction of water with rocks, gases, and organic matter has been critical for the formation of our environment, for its evolution and transformation trends (Vernadsky, 2003).

Second, the common thinking that evolution on the Earth would have begun together with life opens a gap, or even a chasm, between the living and nonliving systems. Meanwhile, both contain water, and this may be a link between the organic and inorganic matter. Water percolating through organisms and rocks leaches them and changes thereby its own properties, mobility, and composition, participates in cycles of different elements, dissolves and forms new substances. Bound or free, water possesses many specific properties (Rassadkin, 2008), and is obviously something that brings together the geological and biological systems, makes them parental, and thus creates a single pivot as a control of the evolution mechanisms (Shvartsev, 2013).



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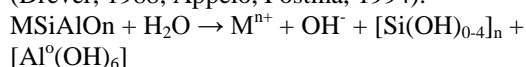
Water itself is enigmatic and underexplored, keeping many secrets of the universe. However, still more striking is its interaction with rocks, especially with igneous rocks, the source material of our planet (Shvartsev, 1991, 1998).

Evolution of the water-rock system

The early Earth is currently considered to have been a magma ocean of basaltic material comprising pyroxene,

low-Si plagioclase (anorthite, bitownite, labradorite), olivine, and minor hornblende. These are exactly the minerals which are never in equilibrium with groundwater.

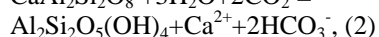
To understand why, look how aluminosilicates dissolve in water by hydrolysis, the reaction being generally (Drever, 1988, Appelo, Postma, 1994).



where *n* are the indefinite atomic ratios; *o* and *t* are the octahedral and tetrahedral sites, respectively; M stands for any metal cation; and the last term of the reaction (M,H)Al^oSiAl^tO_n stands for clay minerals, zeolite, and other secondary phases.

Natural hydrolysis of aluminosilicates always involves H₂O and CO₂ and results in dissolution of all elements to give rise to new products, with their compositions being subject to change in the course of the water-rock interaction.

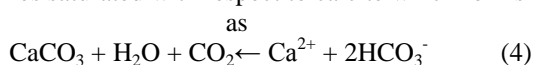
The anorthite hydrolysis reaction producing kaolinite is $CaAl_2Si_2O_8 + 3H_2O + 2CO_2 =$



with the equilibrium constant (K₁), at 25°C, being

$$K_1 = [Ca^{2+}][HCO_3^-]^2 / P_{CO_2} = 10^{5.4} \quad (3)$$

As Ca²⁺ and 2HCO₃⁻ increase continuously, the solution becomes saturated with respect to calcite which forms as



with the constant (K₂), likewise at 25°C,

$$K_2 = [Ca^{2+}][HCO_3^-]^2 / P_{CO_2} = 10^{6.0} \quad (5)$$

Thus, the equilibrium constants in the leaching reactions for both minerals (anorthite and calcite) depend on the same components, i.e., the saturation degrees of water with respect to them are comparable in the same coordinates. As the equations show, calcite precipitates first, and the same follows from the diagram of Fig. 1. Therefore, calcite-laden groundwater remains nonequilibrium with anorthite and continues leaching it. Moreover, anorthite cannot saturate the water at normal conditions because calcite that binds Ca²⁺ and CO₃²⁻ acts as a chemical barrier on the way to its equilibrium

Proceeding from synthesis of largely reported field data, it can be concluded that waters of different compositions and salinities are never in equilibrium with igneous Ca, Mg, and Fe aluminosilicates throughout the crust, from the zone of chemical weathering to that of low-temperature metamorphism (T < 400°C). It is so because the carbonates of these elements (calcite, magnesite, dolomite, siderite, etc.) become chemical barriers to the equilibrium (Shvartsev, 2008).

However, the aluminosilicates of Na and K (albite, muscovite, etc.) can reach equilibrium and precipitate, rather than being dissolved, on long interaction with water, especially at high temperatures and in alkaline environments (Drever, 1988, Shvartsev, 2008).

The above considerations are consistent with geological data. Namely, secondary carbonates are ubiquitous in the crust subject to alteration (chemical weathering, diagenesis, catagenesis, metamorphism, hydrothermal mineralization).

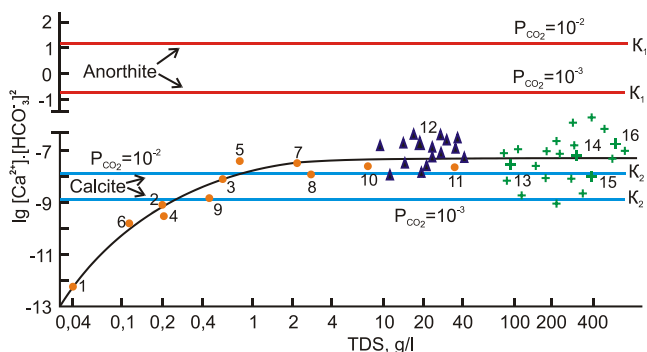


Fig. 1 Saturation of groundwaters with respect to calcite and anorthite vs. TDS

K₁-K₂ are the equilibrium constants (see text). Data points represent average compositions of waters from different regions and zones, namely: circles (1—11) are for Guinea and Côte-d'Ivoire (1), Siberian tundra (2), Senegal (3), zone of temperate climate, generally (4), forest zone of Southern Siberia (5), Finland (6), Central Asian steppes (7), steppes of the USA (8), zone of chemical weathering, generally (9), steppes of the Donets Basin (10), and ocean (11); triangles (12) correspond to waters in petroleum reservoirs of West Siberia; crosses (13—16) mark weak (13), strong (14), very strong (15), and oversaturated (16) brines of East Siberia.

Albitization occurs in diverse continental and oceanic settings below some depths: orogens, cratons, sedimentary basins, provinces of hydrothermalism and volcanism, seafloor, and elsewhere. At the same time, secondary anorthite has never been found though albitization of anorthite is well known (Putnis, 2009).

A wealth of evidence from different areas worldwide

drives at the conclusion that water, wherever it exists, always dissolves some minerals and generates others. Therefore, the water-rock system in the crust is always equilibrium-nonequilibrium and capable of continuous interaction and long geological evolution (Shvartsev, 1991, 2001, 2008, 2009).

It is important that the system 'water – magmatic aluminosilicate minerals' always develops far from equilibrium in the crust, which creates basically new evolution opportunities for it to behave as a progressively self-organizing dissipative structure (Prigogine, Stengers, 1984, Shvartsev, 2013). Unlike cybernetics, nonequilibrium in synergetics makes basis for structure formation and pushes forward the evolution of the system rather than bringing it to collapse. This driving force transforms the irreversible energy (and material) fluxes that arise while the evolving open systems are moving toward equilibrium. The equilibrium-nonequilibrium behavior of the water-rock system is the key agent in the evolution of the mineral matter.

Water that leaches igneous rocks in nonequilibrium conditions creates quite a different environment. First there appear water types of different compositions and new mineral products dissimilar to the original magmatic minerals: feldspar, olivine, and pyroxene give way to kaolinite, montmorillonite, calcite, chlorite, gibbsite, goetite, etc. Water forms this secondary mineral world in perfect harmony with the laws of its intrinsic evolution and energy change. The elements leached from the rocks, in turn, give rise to new mineral compounds with their structure and composition controlled by the changed water chemistry.

Thus, the equilibrium-nonequilibrium water-rock system has its own mechanisms of the intrinsic evolution that runs at any temperature or pressure, rock, water, or atmospheric compositions, physical fields, seismicity, etc. The external factors may influence the rate, intensity, duration, extent, or environment of the reactions but can never stop them, because the system cannot exist without this interaction. Thus, the water-rock system has its intrinsic evolution mechanisms (Shvartsev, 2012), this very property making it similar to a living organism. Or, at least, the property of self evolving is common to both living and nonliving matter.

Therefore, the appearance of water on the Earth means the origin of a system capable of evolving continuously and generating new mineral compounds. They are clay minerals, carbonates, oxides, hydroxides, zeolite, salts, and chemically diverse water types, which have never existed before but, being very stable, have invaded gradually the whole planet. Especially important is the formation of different water types producing diverse geochemical environments (Vernadsky, 2003, Shvartsev, 2013). The water generally thought to be

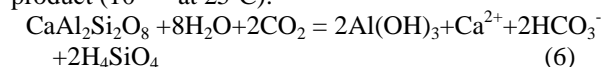
destructive is also a creative agent. Thus, it was water (Shvartsev, 2010) rather than life (Zavarsin, 2000, Dawkins, 2009, Markov, 2010, Koonin, 2011) that has launched evolution on the Earth.

Evolution program in the inorganic water-rock system

Thus, the inorganic water-rock system can evolve in a way similar to the biological evolution. This is by no means surprising, and synergetics has been looking for links between the organic and inorganic matter since long ago (Nicolis, Prigogine, 1977, 1989, Prigogine, Stengers, 1984, Eigen, 1992, Haken, 1996, Prigogine, 1996 et al).

The water-rock system develops in accord with the laws of thermodynamics, in a certain chemical environment, the latter being itself a product of reactions between waters and rocks. The evolution begins with precipitation of the least soluble compounds, with the smallest equilibrium constants, and then there follow ever more soluble secondary minerals, with progressively higher constants. In this system, the water chemistry changes continuously and the phases change successively from one secondary mineral to another.

For example, the reaction of anorthite with water (6) first gives gibbsite, which has the least solubility dot product ($10^{-37.7}$ at 25°C):



Gibbsite forms at the activity coefficient of $[\text{Al}^{3+}]$ as low as $10^{-6.2}$ at pH = 5.0, which is achieved quite soon for the reaction time T_1 (Fig. 2).

Once gibbsite precipitates, it immediately binds Al leached from anorthite into the equilibrium solution, and the Al^{3+} saturation slows down. However, the water keeps reacting

with magmatic minerals in the nonequilibrium system, leaches out all other elements, and becomes saturated with respect to kaolinite (reaction 2). The system reaches equilibrium at the $10^{-4.7}$ activity coefficient of $[\text{H}_4\text{SiO}_4^0]$ (same pH 5.0) and the $10^{-6.2}$ activity of Al^{3+} .

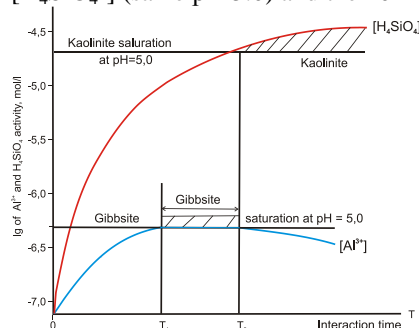
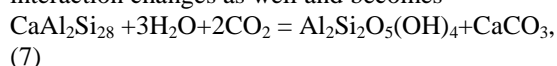


Figure 2. Deposition of gibbsite and kaolinite vs. time of interaction between groundwater and magmatic aluminosilicate minerals

Thus, kaolinite precipitates later than gibbsite but the lag (T_2) is strictly constrained thermodynamically and corresponds to the point of saturation with respect to this mineral (Fig. 2). Of course, Si adsorption slows down after kaolinite has precipitated, but it does not stop because kaolinite can bind a lesser amount of Si than it is leached from magmatic minerals (anorthite and others). That is why other silicate minerals precipitate afterwards as well.

In the same way, saturation with respect to kaolinite does not stop the adsorption of other elements, such as Ca, which increases until the water reaches equilibrium with calcite. Correspondingly, the water-anorthite interaction changes as well and becomes



The precipitation of secondary minerals and the respective complication of the water composition continue as long as the water remains in the rock. Note that time is the critical agent in this evolution process, as it controls the composition of the secondary minerals (Shvartsev, 1998, 2008, 2009, 2012). The reaction time, in turn, depends on the path length and velocity of the water flow. However, each subsequent batch of water percolating through the same rock has the same rate under given PT and geological conditions. Since the amount of water input into the system is likewise definite being a function of rock permeability, all this together means that the water, at some definite point, comes into equilibrium with a definite secondary mineral, and the latter becomes the center of nucleation and accumulation of secondary products with definite compositions.

Thus, the nascent mineral germ falls in a favorable environment being equilibrated and integrated with it. For this reason, the new mineral resists leaching by the subsequent water batches but rather grows with every new drop and invades the surrounding space filling progressively all vugs caved by the water. The size and morphology of the new forms depend on the evolution time of the water-rock system, on the invaded space, the local hydrogeology and geology, etc. Correspondingly, there form either small bodies (like mm calcite veins) or a thick mantle of limestone, laterite, or loess, or oceanic iron-manganese concretions, or any sedimentary rock in general, which can cover vast areas. The course of this evolution remains irreversible unless the rock composition changes dramatically by a critical change in the geological setting or by a catastrophe.

The water-rock system as a whole becomes ever more complex with time. Precipitation of each new mineral means the origin of a daughter system consisting of compositionally different water and a new secondary mineral. Thereby the mother system complicates acquiring new properties, developing new compounds, bonds, and interactions, and producing chemically and

physically new water types. Namely, the water increases in salinity and ionic strength, changes in relative abundances of elements, develops new ion pairs and complexes; the new compounds, in turn, become more complicated in structure and change their migration patterns giving rise to ever new chemical types of water on the Earth, which already count at least hundreds of thousand.

Therefore, besides leaching the rocks, water creates a new mineral world which, being closely related to its environment, is more diverse and stable than the one before. This creative role of water has received almost no attention of scientists and hence eluded further investigation. It is worth reminding in this respect that chemical elements are active only in solutions and that the structure of the latter (the source of information) changes together with the composition. Furthermore, dissolved elements behave as a single whole under the influence of long-range coherent bonds (Prigogine, Stengers, 1984, Nicolis, Prigogin, 1989, Prigogin, 1996). Note that partitioning of elements in newly formed minerals differs from that in the leached rock. Thus water controls the behavior and partitioning of elements and changes the chemical bonds. The critical role of water in element partitioning becomes evident when comparing the relative contents of elements in leached anorthite with that in the secondary minerals (gibbsite, kaolinite, calcite).

Among secondary products formed by the water-rock system, especially widespread are clay minerals (montmorillonite, kaolinite, illite, chlorite, beidellite, and others), which are especially rich with capillary waters. The content of physically bound water in them usually reaches more than 50 wt % and sometimes even 80-90 wt %. According to experimental data of some scientists (Fripiat et al, 1965, 1982, Pitard et al, 1996), such waters differ from water in volume by much higher values of the free energy of formation. Note that the thinner the water film, the higher its energy. Consequently, by its energy parameters, water in the form of thin films is similar to water heated to high temperatures, but by its phase state, it remains a typical liquid.

The above makes it possible to conclude that, while forming, water bound by secondary minerals accumulates solar energy and thus transfers the daughter system to a higher energy level, which ensures a decrease in its entropy (Shvartsev, 2003). In nonequilibrium and irreversible systems, a decrease in entropy may lead not to degradation but rather to complication of the structure, to the emergence of a new branch of its evolution and self-organization, and ultimately to life (Prigogine, Stengers, 1984). From this point of view, when binding a huge amount of water in the process of their formation, clays simultaneously transfer it to a higher energetic level, thus becoming

carriers of huge reserves of accumulated solar energy.

Hence, the energy of the system of water-rock on weathering increases, whereas the entropy correspondingly decreases, which leads, in the context of modern synergetics, to the formation of principally new dissipative structures under the conditions far from equilibrium, which are higher-organized and more complicate in the structural, compositional, and information aspects (Nicolis, Prigogine, 1977, Shvartsev, 2001). The discovery of the abiogenic water—rock system, capable of accumulating solar energy and withstanding the destructive effect of entropy accumulation, is extraordinarily important.

The suggested approach allows formulating the principles of the evolution program in the nonliving matter, which are as simple as any thing of genius: *in conditions far from equilibrium, water continuously leaches minerals in the rock it interacts with, and thereby maintains the concentration of dissolved elements, forms new ion bonds, and gives rise to successively new mineral phases; the latter have basically different compositions, being in equilibrium with the water, and therefore are stable in the respective environment and capable of increasing in volume. The concurrent changes in water composition is the main driving force of the progressive nonlinear evolution of the whole system which becomes ever more complex.*

The formulated program runs irrespective of external forcing, following strictly the laws of equilibrium and nonequilibrium thermodynamics, without any casual failure or error. It is very rigorously designed and durable, like a computer, and can run for infinite time. This program launches the evolution of abiotic systems and acts also in biological systems, wherever water exists. The equilibrium-nonequilibrium state of the water-rock system is the main cause of its internal evolution, time is its key control, while the water chemistry is the govern parameter and the difference of constants in dissolution and precipitation reactions is the thermodynamic variable. It is the difference in relative percentages of elements in the primary and secondary minerals that lies behind the mechanism responsible for chemical differentiation of water and changes in its structure (information carrier), as well as for the origin of new evolution forms and links, including the effects of the daughter systems on the mother ones.

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