

Internal Evolution of the Water-Rock System: Nature and Mechanisms

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Abstract

Self-running internal evolution was thought for a long time to be possible in living systems only but, as the modern synergetic theory implies, it may occur in inorganic complex systems as well. The internal evolution in nonliving systems may be driven by formation of coherent atomic bonds in nonequilibrium conditions, though no material proofs for such a hypothesis has been available. The water-rock system investigated in this study evolves spontaneously due to its intrinsically contradictory equilibrium-nonequilibrium nature. Natural waters can never reach equilibrium with some mafic and ultramafic minerals they dissolve but are in equilibrium with the secondary phases they produce while reacting with the ambient rocks. This is the intrinsic nonequilibrium of water with mantle-derived aluminosilicates that maintains the global-scale evolution of the water-rock system. The evolution continues, without exterior controls, at any time and in any place as long as there are rocks and water, and gives rise to diverse secondary minerals associated with waters of certain compositions.

Keywords: evolution, water-rock interaction, self-organisation, equilibrium-nonequilibrium

1. Introduction

Equilibria in the water-rock system are commonly calculated using thermodynamic methods (Garrels & Christ, 1965), and results of such calculations can be found, for instance, in (Capuano & Cole, 1982; Reed & Spycher, 1984; Nesbitt, 1985; Drever, 1988; Rogers, 1989; Gislason & Arnórsson, 1993; Mohamed et al., 1993; Pawar, 1993; Apello & Postma, 1994; Zamana, 2000; Arnórsson et al., 2002; Gemici & Tarcan, 2004; Gumbardella et al., 2005; Gastrans & Chang, 2010). We have investigated the problem of water-rock equilibrium for years as well (Shvartsev, 1991, 1995a, 1998, 2001a, 2008a; Shvartsev & Dutova, 2001; Alekseev et al., 2005; Shvartsev et al., 2007), specifically, the equilibrium of diverse (fresh, brine, acidic, basic, oil, thermal, etc.) waters, including sedimentary formation water as old as millions of years, with main minerals in rocks.

Calculation of real equilibria in the water-rock system gave unexpected results. For instance, the brines of the Siberian Platform with a mineralization of 300-600 g/l, whose age is hundreds of millions of years and which are virtually immobile, did not come into equilibrium with anorthite, diopside, nepheline, grossular, prehnite, albite, phlogopite, forsterite, cordierite, wollastonite, etc. At the same time, they are in equilibrium with clay minerals, calcite, gypsum, halite, quartz, muscovite, paragonite, analcime, occasionally with albite, enstatite, laumontite, bischofite, tetrahydrite, etc. (Bukaty, 1999; Shvartsev, 2000a).

All of these have allowed us to prove that the water-rock system is an unusual dissipative structure which develops in far from equilibrium and has a number of fundamental properties, among which ability to evolution without participation of live matter. The purpose of the given paper is to show that the water-rock system is capable to internal, independent of external factors, evolution.

2. Equilibrium-nonequilibrium State of the Water-rock System

Analysis of ample published evidence together with our own results prompts that *the water-rock system is equilibrium-nonequilibrium everywhere in the crust* at natural conditions. Aqueous solutions never reach equilibrium with some minerals in igneous rocks (see below) but are, however, in equilibrium with certain secondary phases. Therefore, water can dissolve some minerals and form ever new secondary products. There are neither thermodynamic nor kinetic constraints for this evolution of the system, which is thus internally

consistent and capable of developing spontaneously and continuously for a long geologic time to generate basically new mineral phases and geochemical types of water (Shvartsev, 1991, 2008b; Shvartsev, Ryzhenko, et al., 2007).

Rather than being a particular or a local phenomenon limited in time or in space, water-rock interaction turns out to be a global process of directed changes in which the products have their structure and composition dramatically different from the original ones. For instance, feldspar may transform into montmorillonite, a clay mineral with different chemical and physical properties.

In this transformation, hydrolysis of aluminosilicate minerals is the leading mechanism (Keller, 1957). The compositions of new phases are controlled by the geochemical environment, with different minerals resulting from different processes, namely: mostly clay minerals from supergene alteration; zeolite, chlorite, or serpentine from hydrothermal metasomatism; kaolinite, chlorite, hydromica, or albite from catagenesis, etc. Thus, dissolution in hydrolysis causes transformation of one solid phase into another, the new phase being formed either exactly in the place of the disappearing mineral and replicating its structure (pseudomorphism) or somewhere away from it.

Anyway, two components-water and rock-produce a third one. The conclusion that hydrolysis of aluminosilicates leads to structure loss and system disintegration is partly true, as a new mineral phase forms while some primary mineral is being destroyed; the new phase, together with waters of different chemistries, gives rise to a more complex new structure thus imparting different properties to the evolving system. The new structure involves a new geochemical environment arising as waters uptake chemical elements from rocks and is more complex as it contains additional structural elements that are better adapted to the specific ambient conditions and represent an energetically advantageous state of the system. Therefore, the system proceeds to a more complex stationary state which then transforms, in its turn, into a still more complex one, and so on. This happens, for example, when a weathering profile forms.

The origin of a secondary phase is almost as important as biological reproduction, though the two processes are dissimilar in many ways. The key point is that in both cases a mother system changes dramatically its evolution course as daughter systems spring up. The geochemical environment controls the composition of the nascent secondary phase but changes itself as the latter forms. The changed environment further brings about another phase and again becomes subject to its influence, etc. Being leached, a rock chemically affects its ambience by reducing elements bound in the secondary phase (e. g., Si and Al when kaolinite forms). Thus, the ever changing geochemical environment provides links between the evolving system and its products (Shvartsev, 2009).

Water-equilibrium secondary minerals arise during the whole period of water-rock interaction, not being restricted to local equilibrium. This process is continuous, regional-scale, and nonlinear, this being common to synergetic systems. As the process develops, one association of water-produced secondary minerals grades into another, which corresponds to the known principle of stepwise mineral formation in metallogenic, hydrothermal, metasomatic, supergene, or other processes.

The origin and growth of secondary mineral phases in full accord with the environment is a self-running process going from disintegrated parts to integrity, which according to Ashby (1962) is the key property of self-organizing systems.

Yet, there are other things involved in the issue. Ground waters turn out to be unable of reaching thermodynamic equilibrium with some minerals of igneous (or less often metamorphic) rocks, especially basalt, such as low-silica plagioclase, olivine, and pyroxenes or Ca, Mg, and Fe aluminosilicates. Let us try to understand why.

The anorthite hydrolysis reaction is



with the equilibrium constant (K_1), at 25°C, being

$$K_1 = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / P_{\text{CO}_2} = 10^{5.4} \quad (2)$$

To compare, calcite dissolves as



with the constant (K_2), likewise at 25°C,

$$K_2 = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / P_{\text{CO}_2} = 10^{-6.0} \quad (4)$$

Thus, the equilibrium constants in the dissolution reactions for both minerals depend on the same components but, compared to calcite, the anorthite equilibrium requires (i) an eleven orders of magnitude greater constant and (ii) a squared partial pressure of CO_2 . For this reason, the quotient in the reaction for anorthite is always smaller than that for calcite, even though the contents of elements in the solution are the same. One can compare the two quotients in quite a simple diagram for different groundwater types, as the constants in both reactions are a function of the same components. The dot product $[\text{Ca}^{2+}][\text{HCO}_3^-]^2$ can be estimated for each reaction at a certain value of P_{CO_2} : it is $10^{-0.6}$ for K_1 and $10^{-9.0}$ for K_2 at $P_{\text{CO}_2} = 10^{-3}$; $10^{1.4}$ and 10^{-8} , respectively, at $P_{\text{CO}_2} = 10^{-2}$, etc. Thus, the saturation degrees of water with respect to two minerals (anorthite and calcite) are comparable in the same coordinates (Shvartsev, 1995b).

The estimates of $[\text{Ca}^{2+}][\text{HCO}_3^-]^2$ as a function of groundwater salinity (total dissolved solids, TDS) at different P_{CO_2} are shown in Figure 1. See that fresh groundwater remains unsaturated with respect to calcite unless TDS becomes higher than 0.6 g/l. All saline waters and brines show equilibrium with calcite but calcite-laden waters are never anorthite saturated.

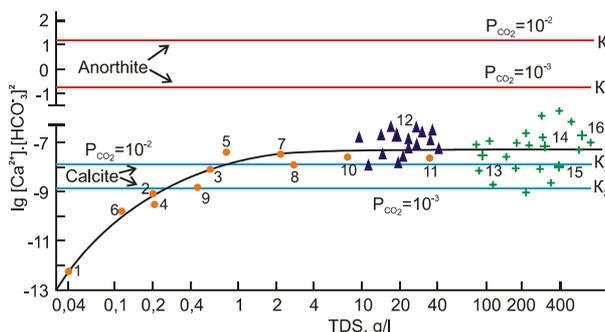


Figure 1. Saturation of groundwaters with respect to calcite and anorthite vs. TDS

K_1 - K_2 are equilibrium constants (see text). Data points represent average compositions of waters from different regions and zones, namely: black circles (1-10) 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 supergene alteration, generally (9), steppes of the Donets Basin (10); open circle is for ocean (11); black 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.

At TDS exceeding 1.0 g/l, the degree of water-anorthite equilibrium remains the same be the salinity 4 or 400 g/l. Moreover, saturation is impossible at normal conditions because calcite that binds Ca^{2+} and CO_3^{2-} acts as a chemical barrier on the way to equilibrium with anorthite. Equilibrium with anorthite is possible only at high $[\text{Ca}^{2+}][\text{HCO}_3^-]^2$ but it is never high because of calcite formation. Therefore, Ca carbonates prevent natural water from arriving at equilibrium with Ca-aluminosilicates.

Consider further an example of forsterite and magnesite dissolution. The reaction for forsterite is



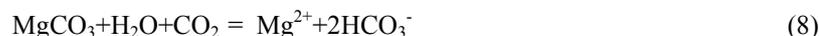
with the constant at 25°C

$$K_3 = [\text{Mg}^{2+}]^2 [\text{HCO}_3^-]^4 [\text{H}_4\text{SiO}_4] / P_{\text{CO}_2}^4 = 10^{-2.48} \quad (6)$$

or

$$[\text{Mg}^{2+}] [\text{HCO}_3^-]^2 [\text{H}_4\text{SiO}_4]^{0.5} / P_{\text{CO}_2}^2 = 10^{-1.24} \quad (7)$$

For magnesite it is



and the constant at 25°C is

$$K_4 = [\text{Mg}^{2+}] [\text{HCO}_3^-]^2 / P_{\text{CO}_2} = 10^{-5.52} \quad (9)$$

As in the case of calcite and anorthite, the equilibrium constants for both minerals likewise are controlled by the same components, and again K_3 is much greater than K_4 (four orders of magnitude) and the CO_2 partial pressure is squared in the former reaction. Therefore, the waters saturated with respect to magnesite never reach forsterite saturation. The latter is impossible in the crust because magnesite binds Mg^{2+} and CO_3^{2-} and thus becomes a barrier to water-forsterite equilibrium (Figure 2). Both figures show calcite (Figure 1) or magnesite (Figure 2) impeding equilibrium of groundwaters with magmatic minerals (anorthite and forsterite, respectively).

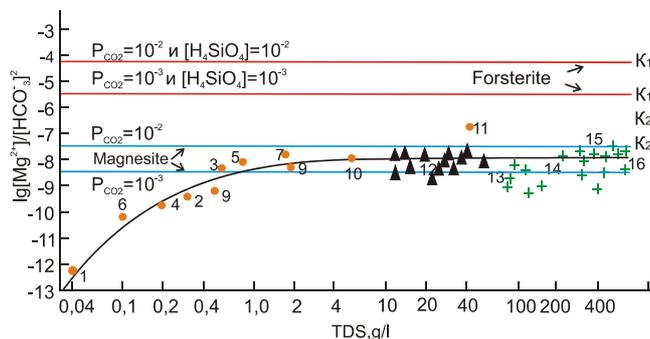


Figure 2. Saturation of groundwaters with respect to magnesite and forsterite vs. TDS
(Legend same as in Figure 1)

Therefore, equilibrium of groundwater with some minerals in igneous rocks is impossible because the leached elements give rise to secondary phases which bind the elements and thus impede the equilibrium. That is why groundwater remains not saturated with respect to these minerals for the whole time of interaction. There are hundreds of such minerals: oxides, hydroxides, silicates, aluminosilicates (clay minerals), carbonates, zeolite, chlorite, sulfates, phosphates, chlorides, etc. The most important Ca, Mg, and Fe minerals of this kind are listed in Table 1.

Table 1. Main minerals of basalt that are dissolved and generated in water-rock system

Element	Minerals continuously dissolved by water	Minerals continuously formed by water		
		Name	Chemical formula	lg dissolution constants at 25°C
Ca	anorthite,	calcite,	CaCO_3	-8.48
	bitownite	dolomite,	$\text{CaMg}(\text{CO}_3)_2$	-17.1
	labradorite	gypsum,	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.58
	hedenbergite, diopside, etc.	fluorite,	CaF_2	-10.6
		Ca-montmorillonite,	$\text{Ca}_{0,17}\text{Al}_{2,33}\text{Si}_{3,67}\text{O}_{10}(\text{OH})_2$	-89.3
		lomontite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$	-98.9
Mg	forsterite,	magnesite,	MgCO_3	-7.46
	enstatite, etc.	dolomite,	$\text{CaMg}(\text{CO}_3)_2$	-17.1
		Mg-montmorillonite,	$\text{Mg}_{0,17}\text{Al}_{2,33}\text{Si}_{2,67}\text{O}_{10}(\text{OH})_2$	-99.5
		talc, chlorite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	-60.7
			$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	-22.4
Fe	fayalite,	goetite,	FeOOH	-32.8
	ferrosilite, etc.	hydroxide,	$\text{Fe}(\text{OH})_3$	-36.0
		hematite,	Fe_2O_3	-83.6
		siderite,	FeCO_3	-10.9
		ferroglaucophane,	$\text{Fe}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$	-16.6
	daphnite,	$\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	-181	
Al	anorthite,	gibbsite,	$\text{Al}(\text{OH})_3$	-32.6
	bitownite	kaolinite,	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-79.4
	labradorite,	illite	$\text{K}_{0,38}\text{Al}_{2,38}\text{Si}_{3,62}\text{O}_{10}(\text{OH})_2$	-108.7
	diopside, etc.			

The equilibrium-nonequilibrium state of the water-rock system is not local but general and ubiquitous. Water, wherever it exists, always dissolves some minerals and generates others. This intrinsically inconsistent state of the system never disappears with time but persists as long as there are rocks and waters. This property is indispensable for the existence of the water-rock system itself and is thus crucial to the evolution of inorganic matter.

Note that there are two evolution patterns in the water-rock system: one in the liquid and the other in solid components. Formation of a secondary mineral requires time for necessary elements to accumulate in the solution (e.g., Si and Al for kaolinite), which is a smooth and continuous process. Formation of minerals is, on the contrary, discrete, and each takes its specific time. Thus, the liquid and solid phases (water and rock) within the same system evolve in different ways: smoothly (continuously) in the former and discontinuously in the latter case.

The permanent nonequilibrium in the water-rock system causes a large-scale process in the upper crust in which water mobilizes chemical elements, transforms rocks into different rocks, and gives rise to new chemical types of water, new mineral phases, and new water-produced mineral associations. This process involving redistribution of chemical elements and formation of secondary minerals with quite different compositions (ores among them), eventually causes global changes to the mineral matter and water out of which our planet had originated, i.e., changes of Earth's crust as a whole (Shvartsev et al., 2007). Therefore, *water and rocks make up a unique system capable of long geological evolution*, even without biotic agents.

It is important that the idea of evolution in inorganic matter is consistent with the theory of synergetics (Prigogine & Stengers, 1984). 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 of the system evolution transforms the irreversible energy (and material) fluxes that arise while evolving open systems are moving toward equilibrium.

Furthermore, they are the nonequilibrium systems that become nuclei of self-organization when new dissipative structures form in open nonlinear complex systems at the beginning of transition from chaos to order (Nicolis & Prigogine, 1977). Self-organization is a well-known phenomenon in the organic life and occurs also in nonliving matter (Shvartsev, 1995b, 2000b, 2001b, 2005, 2007, 2008b, 2009).

3. Internal Evolution of the Water-rock System

The evolution of geological systems has been traditionally assumed to have external controls, such as Earth's cooling, continental growth, reducing extent of tectonic activity, increasing oxidation, air composition changes, biotic effects, etc. (Garrels & Mackenzie, 1971, Ronov, 1980, Yanshin, 1993).

This is not nearly so yet. The water-rock system offers a prominent example of evolution that runs at any temperature or pressure, rock, water, or atmospheric compositions, magnetic field, size and configuration of continents, magmatic activity, etc. Everywhere and always, whichever be the forcing from outside, water dissolves minerals (more or less rapidly), changes the compositions of fluids producing new chemical types of waters, and gives rise to various secondary minerals and mineral assemblages.

External factors can never stop water-rock interaction, though they may influence its rate, intensity, duration, extent, or environment. No force in nature can ever forbid chemical reactions in the water-rock system and prevent water from dissolving primary minerals or from producing secondary phases. The reactions cannot stop unless all water escapes from rock but in this case, however, the system itself will disappear, as well as interaction within it.

This ability of the water-rock system to run by itself prompts the presence of some internal driving mechanisms that must maintain its integrity and isolation, of course on condition of matter and energy supply (the system is stationary and open) (Shvartsev, 2008b). These intrinsic mechanisms allow the system to develop following the thermodynamic laws and to control its own evolution paths and the rates, sequence, and stages of the formation of new products and their compositions, as well as the proportions of elements in the liquid and solid phases, substitutions, etc.

The very fact of running an inherently directed evolution depending on interaction within itself makes the water-rock system so particular and similar to a biological one. The specificity of its evolution (in nonliving matter) is due to geologic-scale duration, continuity of interaction, and impossibility for water to reach equilibrium with all primary minerals.

Geoscientists are well familiar with the results of this evolution, though the links with its intrinsic mechanisms remain unrecognized. The evident results are groundwaters of numerous chemical types, secondary minerals, ore

deposits, diverse formations (such as laterite, clay, loess, redbed, salt-bearing, hydrothermal, ore-bearing, pelagic, flysch, or other rocks), and – on a larger scale – the sedimentary, metamorphic, granite, etc. layers and, perhaps, the crust as a whole. The longer the water-rock interaction, the greater the amount and diversity of secondary products.

Each stage of rock interaction with water produces its own mineral association which gradually covers the geological space, becomes predominant, and defines the aspect of the environment (Shvartsev et al., 2007; Shvartsev, 2007, 2008b).

Let us look deeper into the mechanisms that sustain the internal evolution of the water-rock system. As it was noted above, the nonequilibrium of water with magmatic minerals is the principal driving force. Due to this nonequilibrium, the primary minerals are continuously leached and all chemical elements present in the rocks accumulate in the solution in the beginning of interaction. The rates of dissolution being different in different minerals (Alekseev et al., 2005; Kerrick et al., 1991) the relative percentages of elements always depart from those in the original rock.

While magmatic minerals are continuously being dissolved, the concentrations of elements in the solution are growing and saturation with Fe and Al hydroxides (Table 1) occurs at the initial interaction stage, according to the law of mass action. As the hydroxides precipitate, a part of elements passes from the solution to sediment, thus disturbing the original element partitioning. Iron and aluminum fall out the earliest while all others (including Si, Ca, Mg, etc.) keep accumulating. If the interaction continues, dissolved Si increases and, after some time, the system arrives at equilibrium with formation of kaolinite:



the constant at 25°C being

$$K = 1/[\text{Al}^{3+}]^2[\text{H}_4\text{SiO}_4]^2[\text{OH}^-]^6 = 10^{79.4} \quad (11)$$

In this case the solution loses also Si besides Fe and Al, though all other elements preserve their ability to concentrate in water. Then there appears another feature of difference: Al is bound in gibbsite or böhmite prior to kaolinite saturation but becomes also bound in kaolinite afterwards. Thus, the setting is growing ever more complicated. The question arises which Al minerals will form in this case?

In order to answer the question, one has to compare the composition of kaolinite with those of the leached primary minerals. Namely, Si in igneous rocks is 3.7 times as high as Al, whereas kaolinite contains equal atomic and weight percentages of Al and Si. Therefore, once kaolinite precipitates, the solution becomes depleted more in Al than in Si, hence, kaolinite can form if water contains enough Si, otherwise gibbsite or böhmite will form.

Kaolinite binds all Al coming to the solution but it cannot bind all Si whose input is on average 3.7 times as high as Al, so dissolved Si increases on (Shvartsev et al., 2007; Shvartsev, 2008b). Thus, not every mineral that forms in the water-rock system can bind the whole amount of elements released from igneous rocks. This fact allows some important insights into the mechanisms of internal evolution in the water-rock system.

Meteoric water that falls on igneous rocks (e.g., basalt) dissolves all the constituent minerals. Although there is difference in dissolution kinetics, all chemical elements first enter the solution in approximately the same proportions as they existed originally in the rock. Anyway, the Si input is much greater than Al, though gibbsite forms before kaolinite because gibbsite precipitation begins at a lower activity of aluminum. For instance, at pH = 5.0 groundwater becomes saturated with respect to gibbsite as



already when the activity of $[\text{Al}^{3+}]$ is as low as $10^{-6.2}$, which is achieved quite soon for the interaction time T_1 (Figure 3). Inasmuch as water keeps interacting with the igneous rock, Si unlike Al progressively increases in the solution, which eventually brings the system to equilibrium with kaolinite according to reaction (10) when the activity of H_4SiO_4 reaches $10^{-4.7}$, at pH = 5.0.

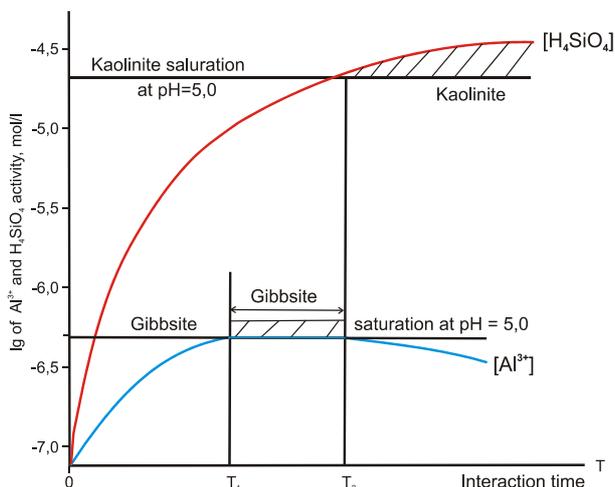


Figure 3. Deposition of gibbsite and kaolinite vs. time of interaction between groundwater and magmaticaluminosilicate minerals

Kaolinite thus precipitates later than gibbsite, after longer water-rock interaction for the time T_2 . Since kaolinite does not bind all Si coming to the solution (see above), the activity of Al^{3+} cannot increase but rather decreases at the same pH, according to the constant of (11), which breaks the equilibrium with gibbsite and the latter, being unable to precipitate, gives place to kaolinite.

Therefore, *gibbsite and kaolinite are competing minerals: they contend for possessing Al supplied to the water from the leached igneous rock*. Gibbsite leads in the beginning of interaction but then lags behind kaolinite while the latter impedes further precipitation of gibbsite. The proof is evident in weathering profiles where gibbsite and kaolinite are always separated and kaolinite lies deeper than gibbsite because its deposition requires a longer interaction time (Keller, 1957; Ollier, 1969).

Interaction between fresh water and magmatic aluminosilicates produces secondary minerals in the following succession: no minerals form in the very beginning at $T_x < T_1$; at $T_1 > T_x < T_2$ precipitation begins with gibbsite; kaolinite forms at $T_x > T_2$; then all other minerals appear in their order (Figure 4). Of course, the process in nature is still more complicated because pH actually changes (most often grows), and for this reason gibbsite neither forms at $T_x > T_2$ nor dissolves. What is important anyway, is that the nonliving water-rock system evolves being driven by its intrinsic mechanisms. Furthermore, *the internal evolution in the water-rock system complies with a single trend of dissolving aluminosilicate minerals and precipitation of ever later phases* (Figure 4).

The explanation of this postulate is as follows. When arriving at equilibrium, say, with calcite (point E in Figure 4) on interaction with the igneous rock it falls into, water will form calcite rather than any other mineral; as elements accumulate progressively in the solution, the latter moves forward to equilibrium with gypsum (point F) rather than back to the earlier equilibrium point of montmorillonite (D).

Thus, as the examples of gibbsite and kaolinite have demonstrated, *a water solution experiences chemical differentiation as partitioning of elements in newly formed minerals changes relative to that in the leached rock, this differentiation being an important indicator of internal evolution in the water-rock system*.

So, water continuously dissolves minerals in the rock it interacts with, and thereby changes its own composition and relative percentages of dissolved elements, also changes the environment, and creates conditions for the appearance of ever new mineral phases. This is the essence of internal evolution in the water-rock system, which lasts for thousands or millions of years.

Note again that this evolution gives rise to quite new minerals basically different from the leached ones (anorthite, labradorite, fayalite, forsterite, etc.), including those the Earth originally lacked, such as gibbsite, kaolinite, montmorillonite, calcite, magnesite, illite, lomontite, etc. (Table 1). This ability of the water-rock system is really striking.

In addition to new minerals, there appear waters of new geochemical types: each secondary mineral forms in water with its composition different from the previous one. For instance, gibbsite, kaolinite, and calcite precipitate from compositionally different waters. Following V. I. Vernadsky (2003), each of these water types

should be interpreted as a separate water mineral. Therefore, each solid secondary mineral must be associated with a certain liquid mineral, or with a certain chemical type of water. Thus, there is a profound genetic link and an intrinsic compositional unity of secondary minerals, waters, and their environment, which is indispensable for the very existence of all these materials. Altogether, they make up a single genetic unit which we suggest to call a *water-mineral formation*. This is a *genetically related association of mineral, organic, and dissolved compounds which are in equilibrium with the parent environment and result from the internal evolution of the water-rock system* (Shvartsev et al., 2007).

Each unit of this kind records a certain evolution stage of the system, which, like a smoothly running machine, produces a formation of a certain composition, for a geologically long time, e.g., laterite at one stage, kaolinite at another stage, and so on. Each new water-mineral formation is a qualitatively more complex system consisting of additional structural elements. Being perfectly ordered and adapted to the environment, they propagate from the local domain of their nucleation and cover ever new geological spaces. This is, for example, laterite in tropic zones of supergene alteration; clay weathering products in zones of temperate climate; iron-manganese concretions in seas and oceans; carbonate calcrete in steppes; redbeds, etc., or thick chloritization and illitization zones in sedimentary basins, or zones of hydrothermal and ore-related metasomatism.

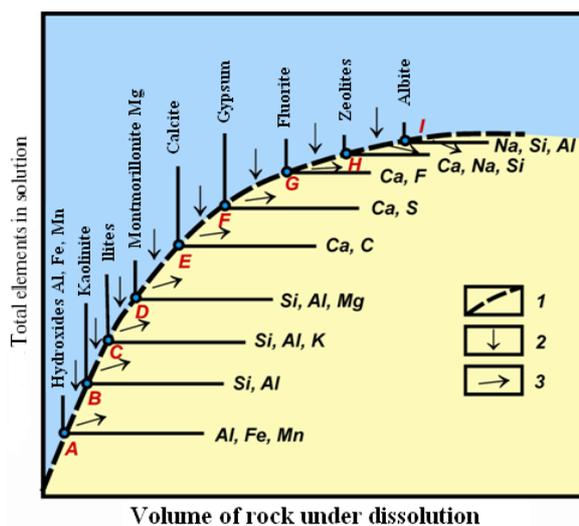


Figure 4. Successive precipitation of secondary minerals during evolution of water-rock system (1) new secondary phases: onset of precipitation, (2) zones of possible water input, and (3) possible cessation of water-rock interaction

Nucleation and propagation of a secondary mineral phase is a typical example of initiation of dissipative structures (Prigogine & Stengers, 1984). Not only the solid becomes more complex, but also its structure does, which is especially important. Progressive salinity increase, nonuniform distribution of elements, growing complexity of compounds and ion pairs, increasing number of minerals which the solution is in equilibrium with: they are all features of development and increasing diversity of structural bonds.

Thus, the water-rock system evolving in a domain far from equilibrium is a source of ordering, growing complexity, and formation of new more highly organized and intricate water-mineral systems, with interaction mechanisms more complex than those that form in equilibrium settings. That is why many geological processes that would seem degrading are not such actually. Chemical weathering, for instance, is commonly assumed to be degradation (disintegration) as it breaks up and thus simplifies structural bonds between minerals and chemical elements. Weathering is often compared with breakup, or at least transformation, of lattice overlooking the fact that it yields more complex new products, e.g., anorthite is weathered into montmorillonite with its structure much more complex than in the primary mineral.

Deposition of a secondary mineral is not just the appearance of a new solid phase, which is important by itself, but rather the origin of a new system “water-secondary mineral”. Moreover, as a mineral precipitates from water, the latter changes its composition and structure in its turn. In terms of synergetics, the onset of precipitation is the bifurcation point where the whole original system (especially water) changes. This happens at the molecular

level as molecules (ions) in water continuously create new structures (new water minerals according to Vernadsky, or new chemical types of water in our terminology).

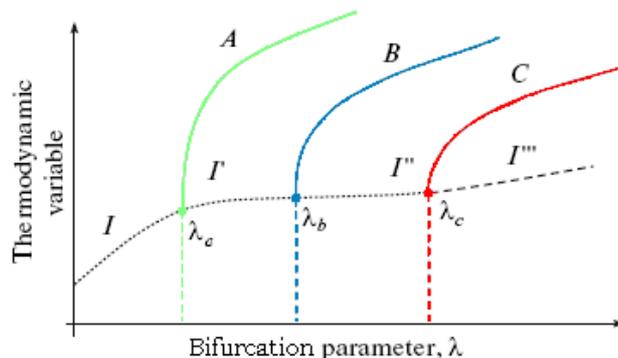


Figure 5. Evolution of a water-rock system in terms of synergetics: initial evolution (I) arrives at unstable state at critical points λ_a , λ_b , λ_c (I^I , I^{II} , I^{III}) and changes trajectory at points A, B, and C (see text for explanation)

Once the solid phase begins nucleating, the water-rock system takes a different evolution path (trajectory) which ends in the formation of a secondary mineral, a new structure, and a new water composition. This is how one mineral successively gives way to others, which is well known as multistage mineral formation and successive substitutions of water types.

The process is infinite theoretically but finite in nature, at least because sooner or later water leaves the rock and the system disappears. The time when it happens depends on external factors (geology, geomorphology, climate, etc.), i.e., the environment can control the lifetime of the system but not its evolution trends.

Viewed in terms of Prigogine's theory (Prigogine, Stengers, 1984), the water-rock system (Figure 5) evolves in time as water chemistry and interaction patterns change though the primary rock remains the same. The slow but directed change in water composition leads to successive precipitation of minerals at the bifurcation points (gibbsite at A, kaolinite at B, montmorillonite at C, etc.), water chemistry being the govern parameter and equilibrium constant being the thermodynamic variable. Figure 5 images the succession in which secondary minerals actually form in nature (Figure 4).

Therefore, while interacting with igneous rock, water produces a new medium dramatically different from the previous one. First, this process shows up in water chemistry changes and appearance of new minerals dissimilar with the primary aluminosilicates: feldspar, olivine, and hornblend give way to kaolinite, montmorillonite, calcite, chlorite, gibbsite, goetite, etc. Later there come bacteria and new landscapes arise, to eventually create a new world (Shvartsev, 2010).

It is important that water forms the new world according to its composition, structure, and environment, and this world is thus *generated by water, in full harmony with the laws of its internal changes and its internal energy*. The water itself and the related chemical environment change under the effect of elements coming from the leached rock, and the structure and composition of the diverse new mineral compounds are defined by *water solutions*.

4. Conclusions

Thus, we have established for the first time the presence of internal, independent of external factors, evolution in lifeless dissipative structure to which the water-rock system belongs. According to Prigogine and Stengers «One of the most interesting aspects of dissipative structures is their coherence. The system behaves as a whole, as if it were the site of long-range forces. In spite of the fact that interactions among molecules do not exceed a range of some 10^{-8} cm, the system is structured as though each molecule were "informed" about the overall state of the system» (Prigogine & Stengers, 1984).

Coherent relations are especially characteristic for solutions. Therefore water, as the main solution of our planet, defines a direction of internal, so all of the global evolution.

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