



## PHASE CHANGES OF WATER AS A BASIS FOR NATURAL WATER-EXCHANGE CYCLES

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### Abstract

*Water draws attention of researchers due to its ubiquity, the role it plays in natural, technological, social and other processes, and the not ultimately comprehended dynamics of its properties, structure, composition, resources, etc.*

*The author, having systematized the literature data and the results of own research, analyzes the role of phase changes and interphase transfers of natural waters in forming water-exchange cycles. It is argued that natural waters are characterized by the effect of phases mixing, determining the unity of all natural waters and high intensity of interphase transfer. Based on this methodological approach, the author specified the scheme of climatic (hydrological) circulation of natural waters. Besides the well-known atmospheric (atmogenic) cycle, the author identified cryohydrogenic, atmolithogenic, glaciogenic and cryolithogenic cycles, calculated the amount of water annually participating in these cycles and the intensity of water exchange in them. This scheme will promote a more focused research of water resources and various water exchange cycles.*

**Keywords :** Phase change of water, interphase water transfer, water-exchange cycles, climatic cycle of water.

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### I. Introduction

The great role of water in biological, geological, hydrological, glaciological, geocryological and many other natural, as well as social and technological, processes promotes special attention and admiration towards this amazing substance. No doubt, questions arise about the nature of water's unique properties, about the causes of its ubiquity. These questions have been posed by researchers at all times. There has been an opinion that the deeper and more comprehensively a scholar studies water, the higher he/she is ranking among the colleagues (Davis and De Wiest, 1964; Derpgolts, 1974; Deryagin, Churayev, Ovcharenko et al., 1989; Drozdov and Grigoryeva, 1963).

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Despite the comprehension of the role the water plays in the life of our planet and the humanity, it remains a phenomenon far from being deciphered. This is especially true for the dynamics of water exchange cycles and, in particular, circulation of natural waters and their unity. For example, B.L. Lichkov repeatedly emphasized that he had not been able to ultimately comprehend the water circulation (Lichkov, 1958, 1962). Analyzing the available schemes of natural water circulation, S.L. Shvartsev points out their narrowness and insufficient account of many driving forces of water cycle (Shvartsev, 1980,2018). All this indicates the necessity to search for new ideas and approaches in the studies of the cyclic nature of global and regional water exchange.

## **II. Methodology and Methods**

Taking into account the interphase water transfer is essential for comprehending the natural water circulation and their unity. It is known that the key feature of any aggregate state of matter is its interaction with its other phases. During phase transfer, the matter is transferred from one phase to another, for example, from liquid to gas (evaporation), from gas to liquid (condensation), etc. Consequently, during the phase change of the first kind, not only the molecular-aggregate state changes, but the matter undergoes interphase transfer, which is the basis of many important natural processes.

Many researchers point out the significance of interphase form of water circulation when studying the processes of water exchange. For example, when viewing the conditions of underground waters formation, V.A. Priklonskiy considered such phase changes as evaporation and condensation, freezing and melting, to be the main types of water circulation in rocks (Priklonskiy, 1958). A.E. Khod'kov and G. Yu. Valukonis placed the transitions of water from one aggregate state to another in the dominant position among all other types of water circulation in a broad sense (Khod'kov and Valukonis, 1968). V.I. Vernadskiy attached great importance to interphase form of water circulation. He specially emphasized that "transitions of water from one state to another – genetic interactions between these mineral types of water, uninterruptedly going on and uninterruptedly reversible, are the main feature of natural waters. The corresponding processes characterize the history of the Earth as a planet" (Vernadskiy, 1960, p.23). Some plenary reports at World Water Balance Symposium (Reading, Great Britain, 1970) emphasized that the urgent theoretical issues of hydrology include, first of all, the study of natural waters circulation and the role of their phase transition in forming various water exchange cycles (Baumgartnes and Reichel, 1972).

Despite the comprehension of a special significance of water interphase interaction in the processes of water circulation, the level of research of this type of water change cannot be recognized satisfactory. Moreover, the sciences of the Earth do not even have unified terms for water phase transitions. For example, in physics and chemical kinetics, the transition of water and any other substance from solid state into gas without the liquid state is called sublimation, while the reverse process –

desublimation. However, in meteorology and glaciology, sublimation is transition of water from gas state into solid, that is, the term is interpreted in the opposite sense. In some sciences, geocryology for example, the term “sublimation” is used in the first sense by some researchers and in the second sense by other ones, creating still more confusion.

The complexity of studying the water interphase interactions is due to the fact that all of its three main aggregate states (ice, liquid water, vapor) are not phase-homogeneous but phase-heterogeneous. In other words, one may say that water is characterized by the effect of phase mixing. For example, any macroscopic amount of ice contains a certain amount of liquid water, as well as various gases, including water vapor. Again, any macroscopic amount of liquid water comprises various gas components in dissolved and sometimes free form. Highlighting this fact, V.I. Vernadskiy wrote, for example, that “in the surrounding nature we do not have any gas not connected with water, or a water solution containing no gas”. He specially emphasized that “the common mass of liquid water forms, together with gases, a dynamic equilibrium common for the whole planet: natural gases  $\leftrightarrow$  natural waters. Gases are dissolved in water—water is evaporated into the Earth’s gas blanket” (Vernadskiy, 1960, p.18). It is important to note that the amount of a certain gas dissolved in water changes depending on the fluctuations of its temperature and external pressure. For example, when water temperature decreases, the amount of gases, dissolved in it, increases; that is, a certain macroscopic amount of liquid water is a kind of absorbent for various gases. When water temperature increases, the amount of gases, dissolved in it, decreases. As a result, a certain amount of dissolved gases is released from liquid water in the form of spontaneous or constant gas emissions. This refers both to molecular gases dissolved in water (methane, hydrogen sulfide, carbon dioxide, etc.), and atomic gases of which a water molecule consists, that is, hydrogen and oxygen. The content of the latter, as well as of their isotopes, also changes depending on the liquid water temperature and external pressure.

Besides gas constituents within a liquid phase of water, one can mark a peculiar presence of its solid phase under certain temperatures and pressure. This is due to peculiar structural properties of volumetric water. For example, it has been found that during transition of water from the solid to the liquid state, the crystal lattice of ice is not destructed completely, and a part of molecules preserve regular structure (Andreev, 2017; Antonchenko, Davydov, and Ilyin, 1991). Further increase of the water temperature reduces the number of such molecules. The complete disappearance of the crystal structure in the liquid phase of volumetric water takes place at a rather high temperature – about 37-42°C.

Thus, the main molecular-aggregate states of water reflect just its macroscopic phase homogeneity, characterizing the properties of a certain phase of water as a continuum. However, from the microscopic viewpoint, the main molecular-aggregate states of water are phase-heterogeneous. Such phase composition of volumetric water is largely explained by the fact that there are no absolutely pure solid, liquid or gaseous forms of water in the natural environment. In

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any macroscopic volume, water is, first of all, a dispersion medium, containing various chemical substances in the form of ionic and other compounds, as well as various trace contaminants in the form of suspended solids, colloidal particles, sols, etc. The increased energy of surface tension on these particles causes forming of peculiar water microphases on their surface, which may differ from its main molecular-aggregate state. Such microparticles serve, in particular, as nuclei of crystallization, condensation and desublimation, i.e. perform the function of phase catalysts during water transition from one aggregate state to another. The phase-heterogeneity of the water main molecular-aggregate state causes various dispersion effects (kinetic, electric, electro-chemical, etc.). All this not only changes the water properties, composition and structure, but also significantly complicates the study of such hydrodynamic systems. This is why the study of, for instance, two-phase gas-liquid systems is carried out mainly in homogeneous approximation, when the parameters and characteristics of the phase-heterogeneous system are averaged through various techniques. This undoubtedly leads to certain errors in calculating the heat- and mass-exchange processes in such systems.

The character of water interphase interactions is especially complicated in rocks, as the above-described phase dispersion of water in any of its molecular-aggregate states is increased by the mechanical dispersion of the rock medium. It is known that all rocks are, first of all, disperse systems (Deryagin, Churayev, Ovcharenko et al., 1989). According to the terminology and principles of the theory of dispersion systems, the water contained in rocks, both in liquid, solid and gaseous states, is usually viewed as a dispersed phase in relation to the dispersed rock medium. However, taking into account the phase-heterogeneous composition of the main molecular-aggregate states of water, as well as the fact that water is a moving component in lithosphere, it is more correct to speak of a disperse water micromedium. For example, film water in the zone of aeration can be viewed as disperse micromedium, being in active interphase interaction with the porous-aerial rock medium. Similarly, the bound unfrozen water in frozen ice-rich rocks should be viewed as disperse micromedium, being in moving interphase interaction with the porous-ice medium of rocks. In particular, this may explain the principle of equilibrium content of unfrozen water and underground ice in frozen rocks, well-known in geocryology and engineering geology (Tsytovich, 1945). The phase transitions of unfrozen water into ice and vice versa take place in rocks, under negative temperatures, under the influence of even slight fluctuations of temperature or external pressure, determining the interphase water exchange.

Though the physical essence of water phase transitions and interphase transfers has molecular-kinetic nature, they underlie many important macroprocesses in various geospheres of the Earth. These cyclic aggregate transformations of water do not only determine the significant changes of soils, rocks and Earth's surface relief, but also largely determine the natural waters circulation, their unity and peculiarity of interactions between hydrosphere, atmosphere, lithosphere and biosphere of our planet. The water phase transitions are related to the features of

water balance of the Earth and its individual regions and territories, formation and dynamics of seasonal and long-term masses of surface and underground ice, snow cover, life cycles of plants and animals, etc.

### III. Results

Taking into account the great role of water phase transitions and interphase transfers in forming various water exchange cycles, the author has stipulated the necessity to review the existing schemes of overall natural waters circulation and to substantiate their unity (Shepelev, 1996, 2001, 2008). First of all, it is necessary to specify the scheme of climatic natural waters circulation, which plays the key role in forming the water balance of the Earth and its individual territories. In the existing schemes, the climatic (hydrological) circulation of natural waters is divided into the atmospheric (atmogenic) cycle and the cycles of surface and underground flows (Alpatyev, 1969; Barri, 1969; Davis and De Wiest, 1966; Drozdov and Grigoryeva, 1963; Voskresenskiy, 1974). The above cycles are based on absolutely different principles. For instance, while the atmospheric (atmogenic) cycle is based on phase transitions of water from liquid to gaseous phase and vice versa, the other two cycles actually characterize just various types or ways of the atmospheric precipitation transportation.

The author proposes, taking into account the water phase transitions and interphase interactions, to distinguish the following water exchange cycles within the climatic (hydrological) circulation of natural waters, besides the atmospheric (atmogenic) cycle: cryohydrogenic, atmolithogenic, glaciogenic and cryolithogenic (see Table).

**Table: Global cycles of the climatic (hydrological) circulation of natural waters and average intensity of their water exchange**

no.	Basic cycles	Amount of water annually participating in water exchange, kg	Average intensity of water exchange, $\text{kg} \cdot \text{m}^{-2} \cdot \text{sec}^{-1}$
1.	Atmospheric	$0.51 \cdot 10^{18}$	$31.5 \cdot 10^{-6}$
2.	Cryohydrogenic	$2.6 \cdot 10^{16}$	$1.6 \cdot 10^{-6}$
3.	Atmolithogenic	$0.2 \cdot 10^{11}$	$0.42 \cdot 10^{-11}$
4.	Glaciogenic	$0.25 \cdot 10^{16}$	$0.16 \cdot 10^{-6}$
5.	Cryolithogenic	$25 \cdot 10^{12}$	$1.6 \cdot 10^{-9}$

### IV. Discussion

The proposed cycles of the climatic (hydrological) circulation of natural waters are determined by different kinds of water phase transitions and interphase transfers.

*Cryohydrogeniccycle* is determined by annual formation of snow cover of the Earth's surface, ice on rivers and water reservoirs, ice crusts and ground ice in the active layer of permafrost and further melting of these seasonal masses of snow and ice during warm seasons.

*Atmolithogeniccycle* is related to evaporation and condensation, sublimation and desublimation of moisture in the zone of rock aeration, forming a peculiar underground atmosphere within which a rather intense water transfer is carried out, determining the interaction between atmosphere and lithosphere.

*Glaciogenicandcryolithogenic cycles* of water exchange are determined not by seasonal, but by long-term climate fluctuations. For example, during colder periods, the volume of solid phase of water in ice sheets and permafrost increases. During warming periods, on the contrary, the resources of the liquid phase of water increase, which is formed by long-term melting of glaciers (*glaciogeniccycle*) and ground ice of permafrost (*cryolithogenic cycle*). Consequently, the influence of these water exchange cycles on the annual balance of liquid natural waters is of trend character, facilitating the long-term increase or decrease of their level and the overall resources. It should be noted here that the surface and underground glaciations cannot be absolutely synchronous due to inertia of permafrost response to climate fluctuations.

The average intensity of water exchange presented in the Table allows making a comparative quantitative estimation of the proposed cycles of climatic circulation of natural waters. The intensity is calculated based on the analysis of the current data on the amount and balance of various types of natural waters on the Earth (Abramova, 1968; Baumgartnes and Reichel, 1972; Ivanov, 1993; Kalinin, 1975; Keller, 1965; L'vovich, 1974; *Mirovoyvodniybalans*, 1974; Pavlov, 1977; Shamov, 2006; Todd, 1970; *Waterresources*, 1986; Zverev, 1993), including the author's own research (Shepelev, 2011). Undoubtedly, the highest activity is demonstrated by the atmospheric cycle of water exchange, which is much more intense than other proposed cycles. The intensity of the *atmolithogenic cycle* is estimated very roughly, as the water exchange function of soil aeration zone is currently very poorly researched (Shepelev, 2011). This testifies to the importance of initiating the research of the features of water exchange in the aeration zone and organizing special monitoring for quantitative estimation of this type of water exchange at the local, regional and global levels.

It should be noted that water phase transitions not only determine various water exchange cycles, but also play a significant role in heat exchange processes. For example, the energy emitted annually during moisture condensation in the atmosphere is just a little less than the radiant energy which reaches the outer boundary of the troposphere (Shepelev, 1996). The energy balance of such global cycles of climatic natural water circulation as *cryolithogenic* and *glaciogenic* ones is also rather high.

The individual cycles of climatic natural water circulation also play a significant role in forming their qualitative composition. For example, during the atmospheric and atmolithogenic cycles, the water is distilled during its evaporation and condensation, which facilitates removal of certain admixtures and dissolved gases, changes in isotope chemical and isotope composition, reduction of ion concentration in water, etc. During cryohydrogenic, glaciogenic and cryolithogenic cycles, when the liquid water phase crystallizes and then the ice melts, the original composition and concentration of water also changes significantly, which may result, for example, in improving the drinking qualities of water and increasing its biological activity. All this indicates that the water exchange climatic cycles, determined by the phase transitions of water, represent the global and local natural mechanisms of its uninterrupted purification and regeneration.

## **V. Conclusion**

The carried out research lead to the conclusion that the phase transitions of water, being very active under the current temperature and pressure conditions of our planet, form the basis of global water exchange cycles. Alongside with that, both the phase transitions of water and its interphase transfers taking place at microscopic level, not only stimulate the manifestation and determine the specific features of these processes at macroscopic level, but also determine the dynamic interaction between various forms of occurrence, state and cohesion of water. The author's assumption that the main aggregate states of water (ice, liquid water, vapor) are not phase-homogeneous but phase-heterogeneous determines the essential principle of unity of the natural waters, features of formation of their resources, balance, concentration, as well as chemical, gas and isotope composition.

It should be highlighted that the phase transitions of water play a determinative role in forming not only the proposed cycles of climatic water exchange, but also certain cycles of geological and biological types of natural waters circulation. Further comprehensive study, from this standpoint, of the cyclic nature of global water exchange is extremely important for understanding the general regularities of interaction and interdependence between various types and state of water and its circulations, as well as for clarifying the role of water in the overall global and regional energy and substance exchange and transformations of these processes under the technogenic activity of the humans.

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