SHORT
COMMUNICATIONS

Geochemical Aspects of Supramolecular Chemistry

A. B. Ptitsyn

Institute of Natural Resources, Ecology, and Cryology, Siberian Division, Russian Academy of Sciences,
ul. Butina 26, P.B. 147, Chita, 672090 Russia
E-mal: inrec.sbras@mail.ru
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Supramolecular chemistry deals with the behavior of molecular individuals and populations: the social and "class" structure of an organized community of individuals, its stability and fragility, and the tendencies of individuals toward uniting and separating, their selectivity, "effective affiliation," their ability to recognize one another, their dynamics, strain, movements and reorientation, their interactions, mutual influence and transformations, as well as the mobility and rigidity between their societies and castes [1]. As the principal functions of supramolecular objects, Lehn [1] pointed to molecular recognition, transformations, and transport.

Although no supramolecular level of material organization has ever been explicitly recognized in geochemistry, systems of this type were examined. Geochemical objects that can be ascribed to supramolecular chemistry include components of dispersed systems: aqueous and biological films, which are characterized by specific interactions.

Molecular recognition is, in fact, the reading (on a supramolecular level) of information that is "written" at the molecular level. Of course, this process is related to energy exchange. Because of this, supramolecular chemistry is regarded as chemical informatics. It is important that, in the region of supramolecular interactions, inorganic systems acquire some characteristics of living systems.

The processes of recognition, transformation, and transportation should depend on the external conditions and, hence, respond to their variations. In this context, it is pertinent to mention another characteristic of supramolecular ensembles: their ability to "read" and process unclear information [2]. This important property enables living, as well as likely biologically rigid, systems to persist and evolve in environments with varying parameters. Consequently, these systems are capable of self-modifying and adapting in response to external influence on the basis of a certain optimization criterion (which was "tailored" in the course of evolution) that maintains the stability of the system.

A provisional model of this self-modification can be a system of the automated stabilization of a process with a computer incorporated into the control contour (Fig. 1). The ideology of this system was published in [3]. Because of the consistent scheme of the direct and reverse feedbacks, this system makes it possible to correct the input parameters immediately in the course of the process in order to bring this process to a certain a priori unknown optimum based on a set of interrelated optimization criteria (Fig. 1, Q_1, Q_2, Q_3). The input parameters of a technological process are specified manually (by the operator) or by a controlling computer. A natural supramolecular system is able to selectively process necessary information from an unsteady information flow.

The third function of supramolecular associates is transport. It definitely affects the state and dynamics of some geochemical and biogeochemical systems. This can pertain to adsorbed water films, natural membranes, geochemical barriers, and biological films, which are characterized by relatively small sizes and occur under a gradient of certain parameters: chemical
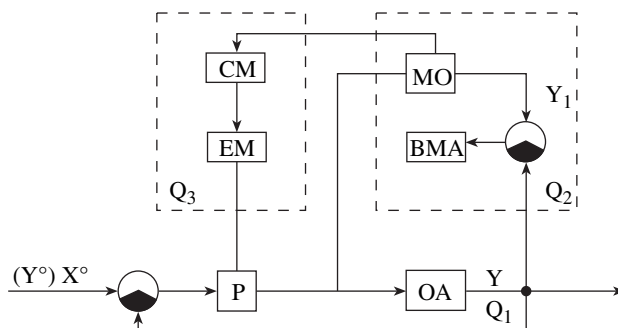

Fig. 1. Schematic representation of automated stabilization with an adjustable model of the object. OA—object to be adjusted; C—controller specifying input parameters; Y_1—desirable value of an output parameter; Y—actual (current) value of the output parameter; CM—computer, EM—executive mechanism, X_0; Y_0—input parameters; MA—block of model adjustment; MO—model of the object.
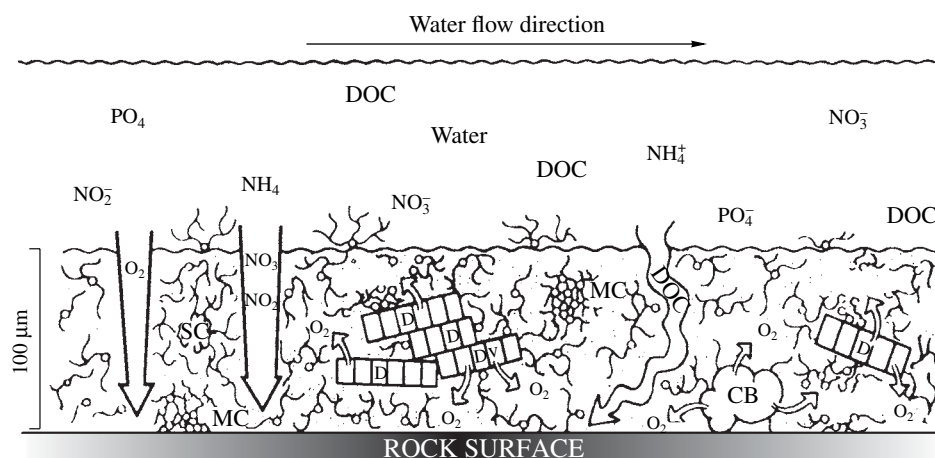
Fig. 2. Schematic representation of a naturally occurring biofilm: CB—cyanobacteria; D—diatoms; DOC—dissolved organic carbon; SC—slimy cells; MC—microcommunities [5].

potential, redox potential Eh, pH, osmotic pressure, etc. Electron-related material transport can occur under a gradient of a redox potential, while proton-related transfer can proceed under a pH gradient. The passage of various particles through a membrane and their sorting can be facilitated by membrane channels: cation, electron, or anion.

Gribov [4] proposed a principally new interpretation of information (or energy) transfer within molecular systems on the basis of the electron-oscillation mechanism.

The hierarchical ascent from the atomic nucleus to an atom, molecule, and supramolecular ensemble is coupled with the complication of the system and a decrease in the interaction energy. Each of the levels is characterized by certain mechanisms of information transfer, which mediate the direct and reverse feedbacks and maintain the unity of complicated systems. When a more complicated system is formed, information flows from its discrete constituents, mingle, and form new structures and new characteristics. Systems at each step of the hierarchical ladder are characterized by certain sets of components: these are nucleons for an atomic nucleus, nuclei for an atom, atoms for a molecule, and molecules for a supramolecular ensemble. Correspondingly, the bond strengths between the components decrease: these bonds are enormously vast for a nucleus, fairly significant for an atom, strong for a molecule, much weaker for a supramolecular ensemble, and are likely still much weaker for systems of higher hierarchical levels.

As was mentioned above, one of the geochemical objects of supramolecular chemistry is films or cyanobacterial mats. Various cyanobacteria species (their number exceed 1500) can participate in mineral-forming processes, form geochemical barriers (oxidation, reduction, H_2S, alkaline), can consume H_2S and H_2, and are among the main producers of organic matter.

Cyanobacteria exist on Earth from its earliest evolutionary stages [5]. Their traces were found, for example, in Australian siliceous rocks dated at approximately 3500 Ma. Cyanobacteria encompass soil-dwelling and aquatic species, and the latter include planktonic and benthic ones. A cyanobacterial community is considered to be an independent taxon.

Biological films have a layered inner structure, with alternating layers of microorganisms and minerals, for example, carbonate. Because of photosynthesis, the uppermost layer is enriched in oxygen, whose concentration rapidly decreases with "depth" inward the film, and the hydrogen sulfide concentration simultaneously increases. The redox potential Eh changes from +200 to −200 mV over a distance of only 10 mm, and the pH correspondingly changes from 9.6 to 7.0. Any drastic changes in Eh and pH in the biofilm result in the alternation of different barriers (such as oxidizing and H_2S) within a short distance, and this, in turn, forms unusual zoning. Oxidizing environments suppress the activity of cyanobacterial biocenoses. Biological films can develop on very different surfaces in contact with water. A scheme of such a film is presented in Fig. 2 [5].

The geochemical roles of bacteria are also very diverse. Their activity is thought to be responsible for the origin of certain sedimentary rocks: phosphorites, carbonates, and others. This is caused by the effect of biogeochemical barriers. Bacteria may serve as catalysts during the formation of authigenic silicates. The list of minerals that can be generated with the participation of bacteria is continuously appended [6] and includes carbonates (calcite, aragonite, and monohydrocalcite), phosphates (dahllite, francolite, strunzite, vivianite, and others), sulfates (jarosite), iron oxides (magnetite and ferrihydrite), sulfides (pyrite, hydrotroilite, sphalerite, wurtzite, and others), quartz, cristobalite, pyrolusite, phyllosilicates, and feldspars. It was noted that mineral-forming processes in modern hot
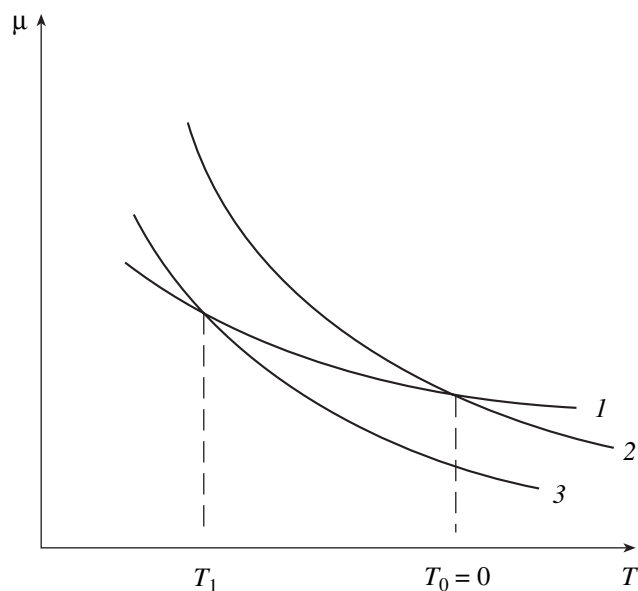
μ

Fig. 3. Temperature dependence of H_2O chemical potential in (*1*) ice, (*2*) free water, and (*3*) bound water.

characteristics. Our knowledge about these objects still abounds in blind spots and disputable aspects.

The theory of the recognition of selective bonding in molecular aggregates is a clue for understanding the process of selective sorption and, perhaps, also ion exchange, which can be of significant applied importance, for example, the production of selective flotation agents, development of sorption filters, etc.

Obviously, the supramolecular branch of hydrogeochemistry and, particularly, biogeochemistry is highly promising.

springs have very high rates (minutes to hours) when participated by bacteria.

The organic matter of cyanobacterial mats can, in principle, serve as material from which oil is produced. This raises the possibility of the discovery of hydrocarbon resources in Precambrian rocks. It is quite probable that rare elements and REE can be efficiently concentrated at the biogeochemical barriers of cyanobacterial mats. It is also worth mentioning the activity of element-specific bacteria, which are able to accumulate various elements: Fe, S, and others. Bacteria undoubtedly take an active part in the origin of weathering crusts. Iron- and sulfur-oxidizing bacteria can drastically intensify the development of oxidation zones and facilitate the dissolution of several metals in aqueous solutions. This mechanism is currently widely utilized in the technological processes of the bacterial leaching of Au, Cu, and other metals.

Another geochemical type of geochemical objects studied by supramolecular chemistry is aqueous films adsorbed on mineral surfaces, which were described in numerous publications [7–11]. Both biological and inorganic aqueous films are characterized by an unusual state of the matter, which is structured under the effect of chemical and physical forces on a supramolecular level. Consequently, aqueous films show a lower water potential (Fig. 3) and all related

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