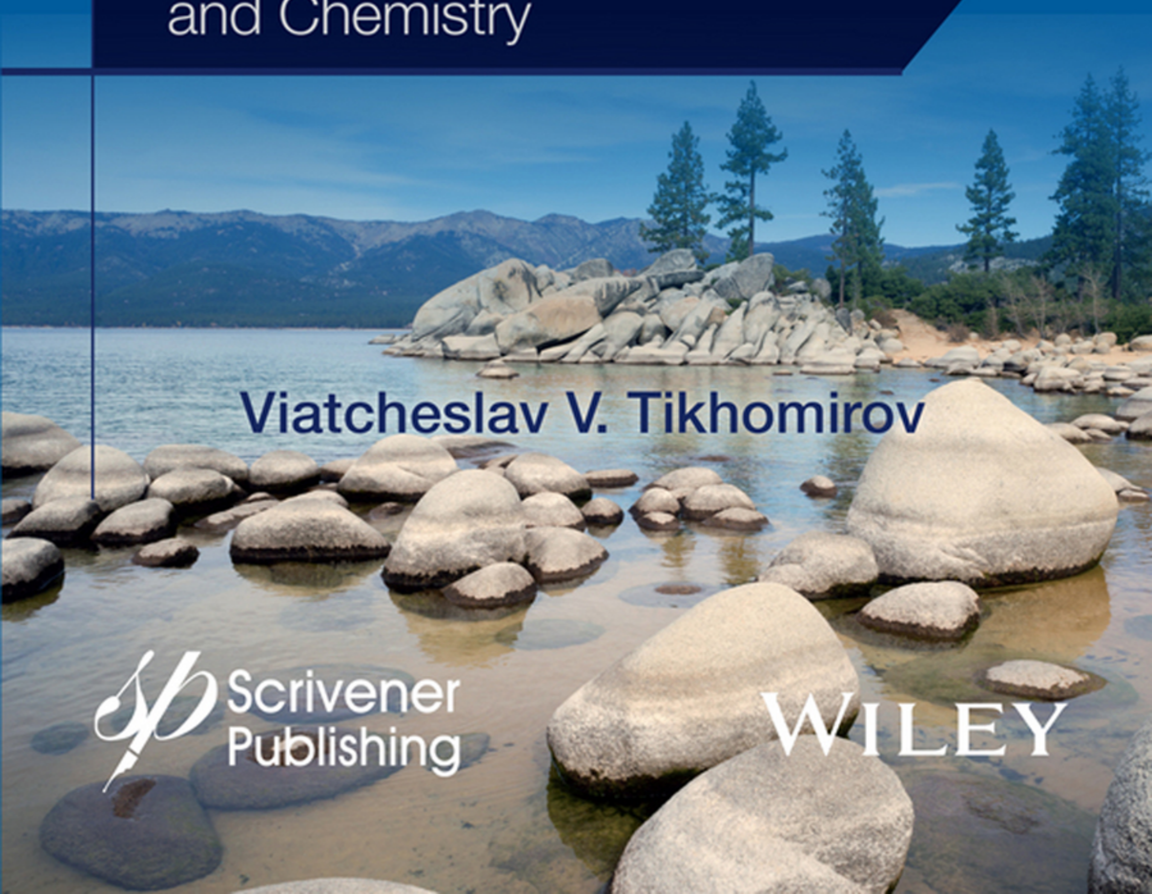
VOLUME 1

Hydrogeochemistry Fundamentals and Advances

Groundwater Composition and Chemistry



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Volume 1: Groundwater Composition and Chemistry

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My loved women,
to my mother, wife and daughter
dedicated!

Contents

Preface

This textbook includes main sections of hydrogeochemistry, methods of its study, terminology and concepts. The textbook is based on the experience and traditions of teaching hydrogeochemistry at the Hydrogeology department of the Sankt-Peterburg State University. These traditions were laid by a brilliant lecturer and scientist Vera Sergeyevna Samarina who taught hydrogeochemistry over a period of almost 40 years and wrote one of the first textbooks in this discipline. These traditions were extended by M.A. Martynova, E.V. Chasovnikova, M.V. Charykova and other lecturers in the department.

The textbook includes three sections. In the first section study methods are reviewed of the geologic medium's hydrogeochemical state. Provided in the section are concepts of analytical ground water composition and properties, and methods of their study. At the conclusion of the section are analysis methods of collected materials, methods of constructing maps, cross-sections and models of ground water geochemical state. The second section introduces spontaneous processes in the water connected with the disruption of thermodynamical equilibrium. The processes are reviewed in consideration of a complex geologic environment, in order to give the idea of methods used for their numerical modeling. The last section reviews external factors of the formation of ground water composition in different climatic and geologic conditions. The spotlight of the section is on the formation of the ground waters' composition, their interaction between themselves and with enclosing rocks. Figuratively, if we view the ground water as a living organism, the first section is discussing its anatomy, the second, its psychology and physiology and the third one, its destiny.

As Hilbert Newton Lewis wrote in the foreword to his *Chemical thermodynamics*, "…a textbook is sort of a restaurant where one can stay his/her hunger without thinking about complex and meticulous processes forming the raw products…" This work is exactly such a textbook and does not pretend to argue controversial hydrogeochemical issues. The main objective of the textbook is to serve previously prepared courses in due order, maximum catchy and gustable. For this reason, the main effort was not the search after truth but systematization and presenting already established provisions.

The publication of this textbook was made possible due to the help by all members of the hydrogeology department of the Geologic faculty at the Sankt-Peterburg State University. I am especially indebted to the department head P.K. Konasavsky and to A.A. Potapov who took upon himself the ungrateful labor of reviewing. I would like also to express my sincere gratitude for the advice, help and useful critique to M.A. Martynova and A.A. Schwartz.

Introduction

Hydrogeochemistry is a science of ground water composition and properties. It studies the distribution of ground water of different properties and composition in the conditions of geologic medium, as well as causes and effects of changes in these properties and composition as they affect the economy. Hydrogeochemistry facilitates the understanding of numerous geologic processes and conditions for the formation of economic deposits, and it solves problems of engineering, geology and ecology. Over time, forecasting and controlling ground water properties and composition has grown more significant in the environment of continuously increasing technogenic effect on nature.

Whereas geochemistry deals with chemical elements' distribution in the composition of the Earth as a whole and hydrochemistry – in the composition of any natural water, hydrogeochemistry concerns the same in the composition only of ground water.

All study methods in hydrogeochemistry lean on the approaches developed in fundamental sciences such as mathematics, chemistry, physics, geology and biology. Thus, to study hydrogeochemistry one needs to have deep knowledge in the basics of these sciences, in particular thermodynamics, chemistry and in recent times also mathematic modeling.

Hydrogeochemistry as an applied science acquired its name relatively late, in the 1920–1930s. Its emergence was caused by the interest to ground waters and by progress in analytical chemistry, which enabled distinguishing ground waters by the composition. Currently hydrochemistry is a scientific discipline of a great practical value. It provides the knowledge necessary for solving problems in lithology, geochemistry, mineralogy, geophysics, exploration for economic deposits, engineering geology and ecology.

HYDROGEOCHEMISTRY: PREHISTORY AND HISTORY

The emergence of hydrogeochemistry as a science was preceded by a thousand-year long prehistory when the concepts of substance of the water, its properties and composition formed. These concepts, similar in appearance, but different in the taste, color and smell of ground waters had been developing way before the emergence of fundamental sectoral sciences (physics, chemistry, geology, etc.)

This prehistory may be broken down into three basic stages: I. pre-Aristotelian, II. Aristotelian and III. post- Aristotelian.

I. The first stage comprises tens of millennia in the human history and ends up with the emergence of ancient natural philosophy. At this stage the water was treated as an animate subject, as deity, and as a terrible element. For this reason the interrelations with the water were initially greater than of a moral nature as with a living being. Only by the very end of this stage was the water treated as an object – the substance with its inherent properties.

People always used water. From the time immemorial they knew that not any water is suitable for their existence, and they knew how to discern it by the quality. So, many applied problems of the present-day hydrogeochemistry were important and were being solved way before its emergence. Most pressing of these issues was undoubtedly the search of waters suitable for drinking, therapy, livestock watering, and irrigation. These qualities were determined sensorily, i.e., by the appearance, smell and taste. Already at that time the people distinguished among natural waters fresh (the Slavs called it *nonfermented, fresh*; the British, *fresh* and the Germans, *frisch*), sour (in English; in German, *sauer*), sweet (Slavs: *sladka voda*, *slodko woda*; British: *sweet*; German: *suss*; French: *sucre*), salt (English: *salt;* German: *salzig*; French: *sale*) and bitter (Slavs: nasty, bad, worse; British: *bitter*), etc. Such separation of the ground water by taste parameters may be considered to have been the oldest hydrochemical classification. In the areas where there were no fresh-water rivers or lakes the people were looking not just for the water, but for a fresh, sweet ground water. The experience of looking for such waters and improving their qualities was undoubtedly transferred from one generation to the next and accumulated. This experience was valued especially highly in deserts or steppes. This is indicated by the Biblical lore of Moses' miracles during the 40 year-long exodus of the Israelis from the land of Egypt through parched deserts of the Sinai Peninsula. "*22:* So Moses brought Israel from the Red sea, and they went out into the wilderness of Shur; and they went three days in the wilderness, and found no water. *23:* And when they came to Marah, they could not drink of the waters of Marah, for they were bitter: therefore the name of it was called Marah[1]." On advice from the Lord, Moses added wood into the water, and the water became sweet. A salt water spring under this name is known currently on the western shore of the Sinai. The Arabs call it Ayun Musa, i.e., the spring of Moses. Its water has a bitter after-taste due to the elevated content of calcium and potassium sulphate. It may be assumed that Moses threw in the water branches of the elvah shrub, which was growing in the Sinai Desert. These branches contain a lot of oxalic acid, which removes the calcium and potassium sulphate from the water.

In those times, almost any liquid was called water, any gas was called air, and any solid substance was called earth. Fire was the most efficient means of primeval chemical analysis. Whatever burnt seemed as if it was turning into air and earth. This formed the idea of four elements of the universe: earth, water, air and fire. The people still did not see a substantial difference between ice and stone. The word crystal meant ice for the ancient Greeks. Out of the general range of customary matter fell only smelted metals. For this reason the first discovered elements were metals: gold, silver, copper, iron, tin, mercury and lead, which ancient astrologers associated with the sun and major planets.

Eventually the capacity of water to convert to air when heated, or to earth when strongly cooled was noted. Perhaps this exact experience of turning the water into earth and into air became a cause of the water losing its animateness and becoming a substance.

In connection with these, the issues of the essence of water and of the nature of its properties became essential. As described by Classical Greek philosophers, first attempts to answer these questions came down to us by Thales of Miletus (625–547 BC) and Plato of Athens (427–347 BC). They believed in the existence of the primary source of all matter on Earth. This

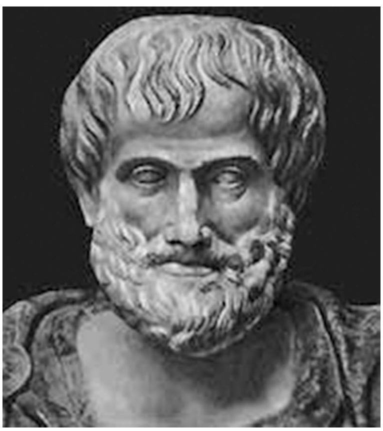
[1] Exodus, Chapter 15, verses 22 and 23 (King James Bible).

philosophical concept, later called ***naive monism,*** became commonly recognized by Classical Greek philosophers. According to this philosophy, the "primary substance" existed, from which emerged all other matter. Thales believed that such primary substance was water.

A different viewpoint on the nature of matter was held by Leucippus of Abdera or Miletus (Vth century BC) and his student Democritus of Abdera (460–370 BC). Contrary to Plato's ideas they rejected infinite divisibility of matter and believed that the water also is composed of an infinite number of indivisible particles of matter - atoms, which are not destroyed and do not emerge. However, these atomistic ideas have been forgotten for two millennia.

A belief existed in those times that land was floating in the ocean and that fresh ground waters in the springs formed from the sea water. Perhaps, this question: how the salt water under the ground converts into a fresh water, began the formation of initial hydrogeochemistry concepts. Plato believed that salinity and bitterness of water simply do not percolate through earth.

II. The second stage covers almost two millennia of indisputable authority of Aristotle (384–322 BC). His influence spread with translation of his works into Syrian, then Arabic and in 12^{th} century into Latin.



Aristotle (384–322 BC)

Aristotle, remaining within the framework of naive monism, attempted to explain element transmutation of one into the other. His doctrine was based on the concepts, not of atoms, but of four pairwise opposite properties whose relative content determined the essence of the elements: humidity and dryness, cold and heat. Variations in quantitative ratios of these properties in the composition of matter determined the transmutation of one substance to the other. The water possesses the largest content of humidity and cold, the air, of heat and humidity. He maintained that different combinations of these properties are responsible for all variety of matter on Earth. Aristotle believed that matter can transmutate into each other, and this capability is due to the existence of some principium (the ether or the fifth essence, *quinta essentia*).

Besides, Aristotle no longer associated the origin of fresh water directly with the sea water. In his belief the underground fresh water formed from the air in cold voids of the Earth. This made him the first one to formulate a very important concept related to the formation of the ground water composition: "Waters are of the same qualities as the earth, through which they flow."

Aristotle's idea that by manipulating the properties, it is possible to convert one substance into another, rendered tremendous influence on the evolution of the natural philosophy and facilitated the emergence of alchemy. In Europe Aristotle's doctrine became popular only in the 12th century, due to the efforts of Albert the Great (around 1193–1280) and Thomas Aquinas (1225–1274). Thus began the Christianization of Aristotle's doctrines and their penetration of Catholic theology. At the same time alchemy became very common in Europe. Its main purpose was finding of the "philosopher's stone" for forming gold, silver, longevity potion, universal solvent, etc. The main means of affecting matter were fire and water. One of the major tenets of alchemy said: "Bodies do not act unless they are dissolved." A consequence was active studies of water properties, its capacity to dissolve other matter and to convert into air and earth. Alchemy achievements facilitated the emergence of metallurgy, glass works, manufacturing of paints and discovery of new elements. However, ideas about the essence of natural water did not change. According to Nicolas Flamel (1330–1417?), alchemists continued to believe that "the dissolution is not the absorption of the bodies by water, but their transmutation or conversion of the bodies into the water, from which they were originally created."

Georgius Bauer (Agricola) (1494–1555) developed the fundamentals of chemical analysis and processing of copper, silver and lead ores. He noted the important role of ground water in ore formation and suggested that ores were "congealed sap of the Earth," i.e., formed from ground water. And in his work "On the place and causes of underground (flows)," published in 1546, he proposed that ground waters formed not only from percolation of rain, river and ocean waters but, very importantly, due to congealing of underground vapors. Herewith he first came up with the idea that the water penetrating deep under the surface could turn into vapor, which rose to the surface, congealed and again formed ground water.

Great Discoveries of early XVIth century facilitated the studies of ground water distribution on Earth and its circulation cycle. In 1569–1580 Jacques Bessonn and Bernard Palissy shaped the modern concept of water circulation cycle on Earth. In 1634 René Descartes (1596–1650) in his "Treatise on light," formulated the concept of Earth's spherical zoning: Earth is composed of flaming liquid core, solid crust and the layers of liquid water and atmosphere. In 1644 C. Claramons made a first estimate of the water amount in the ocean. But the ideas of the nature of water per se practically did not change.

The terms "air" and "vapor" initially were used interchangeably. Galileo Galilei (1564–1642) and René Descartes were among the first who distinguished between them. Jan van Helmont (1579–1644) who introduced the notion of "gas" proposed to consider vapor/steam as a transitional stage of water turning into air.

René Descartes stated that "there is always equal amount of salt" in the sea. His "*Principia Philosophiae,*" published in 1644, included the section "On the nature of water and why it easily converts to the air and to the ice." He tried to explain the transmutation of a fresh water into a salt one by suggesting that it is composed of flexible and rigid particles. If these particles, suitably tied with one another, are separated, some of them (flexible) produce the fresh water and some others (inflexible), the saline water. He assumed that in the process of filtration inflexible particles are retained and the saline sea water becomes fresh. Soon thereafter, in 1674, Robert Boyle (1627–1691) established constancy of the marine water salinity. His determination of the average ocean water salinity differed from the current one just by 1%.

Robert Boyle (1627–1691)

Nevertheless, Jan van Helmont still believed that "all bodies (which considered to be mixed), whatever were their nature, opaque and transparent, solid and liquid, similar and dissimilar (as stones, sulfur, metal, honey, wax, fat, ocher, brain, cartilages, wood, bark, leaves, etc.), are made up actually from the simple water and can be completely converted into a tasteless water, at that not even the smallest fraction of the earthly world will remain".

In the second half of the XVII[th] century through the studies of Robert Hooke (1635–1703), Christian Huygens (1629–95), Robert Boyle, Isaac Newton (1643–1727) and others, the boiling temperature of water and melting temperature of ice were determined. In 1772 Jean-André Deluc (1727–1817) found that the water reaches maximum density at a temperature around 4 ^{0}C, and James Watt (1736–1819) forced the steam into working for mankind. Nevertheless, concepts of the nature of water per se practically did not change. And the inventor of a universal steam engine, James Watt, believed that "the air is a modification of the water."

III. The end of domination of Aristotle's ideas was defined by Robert Boyle (1627–1691) when he turned to atomistic ideas of the ancient philosophy as related by Democritus of Abdera. Based on these ideas Robert Boyle created the "corpuscular philosophy" and introduced a concept of the "element" as a minimum indivisible component of any substance, and "chemical analysis." Another large feather in Boyle's cap was the affirmation of a leading role of expertize and experiment as a correctness criterion of any theory. He wrote that, "researchers would render the greatest service to the world if they devoted all their forces to manufacturing experiments, collecting observations and did not establish any theories without preliminarily verifying their veracity through the experiment." His efforts resulted in qualitative change of study techniques. Thereafter chemical experiments were conducted with accurate measuring of the mass of interacting matter. This enabled R. Boyle to prove that fire is not a substance but only a result of burning with the participation of the air.

In the XVIIIth century special attention attracted curative properties of the ground water. Mineral water treatment became fashionable. As the health resort business tempestuously grew, plenty of attention was devoted to the search of mineral ground waters and study of their properties, composition, and formation conditions. In Russia, first scientific interest to mineral waters was associated with the name of Peter the Great. It was he who attracted attention to the need for exploring national natural resources, in particular searching and utilization of curative waters. He also was the originator of first expeditions for the study of Russia's natural treasures and organizer of health resorts on mineral waters. In 1719 first state health resort "Marcial waters" was launched in Karelia. A great role in studies of ground waters in Russia belonged to the Russian Academy of Sciences founded by Peter I and its expeditions for the study of natural treasures in Russia. Ground waters were studied by Stepan Petrovich Krasheninnikov (1711–1755), Ivan Ivanovich Lepekhin (1740–1802), Nikolay Yakovlevich Ozeretskovsky (1750–1827), Nikolay Petrovich Rychkov (1746–1784), Vasily Fedorovich Zuyev (1754–1794), Peter Simon Pallas (1741–1811) and others. Their efforts resulted in the formation in XVIII century of first scientific concepts of ground waters in Russia, which formulated in his works "On layers of Earth" and "On the birth of metals from shaking of Earth," by Mikhail Vasilyevich Lomonosov (1711–1765). In 1785, in France a first *Thesaurus of all mineral springs of the realm with their brief descriptions* was published. But even then, the concepts of the nature of water had hardly changed.

However, measuring the mass of combustion products in the air discovered inexplicable loss of matter. A German physician, Georg Ernst Stahl

(1659–1734) explained this loss by the existence of some matter with negative mass. He named this substance phlogiston. The search of this enigmatic substance had a definitive significance in the evolution of concepts of air composition and facilitated the discovery of hydrogen and oxygen.

Many scientists tried to catch and study this mysterious phlogiston. At last, in 1766 the Englishman, Henry Cavendish (1731–1810) made it. He discovered a substance similar to it. Later this substance, for its exceptional role in the formation of water, was called hydrogen (Latin *Hydrogenium*). Five years later, in 1771, in the work "On the nature of waters" a Frenchman, Antoine Laurent Lavoisier (1743–1794), proved that the water and earth could not convert into each other. The same year, a Swede, Carl Sheele (1742–1786), and in 1774 an Englishman, Joseph Priestley (1733–1804), independently discovered oxygen. They informed A.L. Lavoisier about their discovery, and he found that their substance was a component of the air, acid and many other compounds. In 1777 discoveries of oxygen and nitrogen determined the air composition. These discoveries allowed A.L. Lavoisier to reject the theory of phlogiston and assert the validity of the law of conservation of matter. In 10 years, in 1783–1785 the same indefatigable A. Lavoisier proved that the water was composed of hydrogen and oxygen and cannot convert to the air and back. These successes in chemistry enabled Alexander von Humboldt (1769–1859) and Joseph Louis Gay-Lussac (1778–1850) in 1805 to determine the chemical formula of the solvent in water composition: H_2O.

Antoine Laurent Lavoisier (1743–1794)

Thus, it was proven that the natural water is a complex solution dominated by the compound of oxygen and hydrogen, H_2O. For this reason further studies of ground water directed to the determination of its dissolved matter were closely associated with successes in chemistry, especially analytical chemistry.

In 1804 John Dalton (1766–1844) published a first table of atomic masses. In 1807–1808 an English physicist, Humphry Davy (1778–1829), discovered sodium and potassium, and he proved the elementary nature of chlorine. The circle of studied atoms rapidly expanded. In 1865 Dmitry Ivanovich Mendeleyev (1834–1907) established periodical law of chemical elements having thereby determined the boundaries of this circle. A little later (in 1896) a French physicist, Antuan Anri Bekkerel (1852–1908), discovered radioactivity, i.e., capacity of some atoms to convert spontaneously into other atoms. This discovery drew attention to radioactive elements, first of all uranium, thorium and radium and products of their decay. By 1911 for 12 places in Mendeleyev's periodic table competed around 40 elements with different radioactive properties. In an attempt to solve this problem, in 1910 Frederic Soddy (1887–1956) came to a conclusion of the existence of elements with similar properties but diffeent atomic mass.

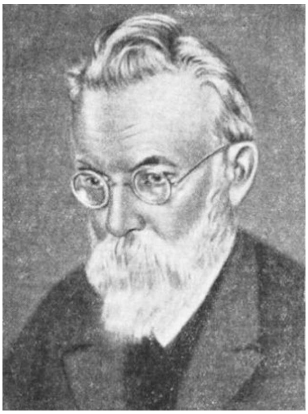
In 1913 he proposed to call such atoms isotopes. Soon thereafter it was proven that beside stable isotopes there may also be radioactive ones. In 1929 William F. Giauque (1895–1982) and a student Garrick Johnston (USA) identified three stable isotopes in the atmospheric oxygen, and in 1932 Harold Clayton Urey (1893–1981) discovered deuterium and heavy water.

At the same time analytical chemistry methods were being developed and improved, which enabled the determination of individual element contents in the composition of various natural matter, including the natural water. The ground water composition was initially studied in order to search for new elements and identify their properties and distribution. Then, early in the XIXth century, appeared the interest to the ground water composition associated with the study of their balneological properties. Gradually the scope of studied ground waters and components in their composition expanded, which facilitated the formation of concepts about the ground water as a composite solution.

In connection with these, at the same time, there appeared theories of the structure and properties of water solutions of electrolytes, and of solution and precipitation processes. The theory of electrolytic dissociation proposed in 1887 by Svante Arrhenius (1859–1927) turned out to be especially fruitful. In 1923 Peter Joseph Debye (1884–1966) and Erich Armand Hückel (1896–1980) proposed a statistical theory of diluted strong electrolytes, which facilitated the transfer from simple concentration of electrolytes to thermodynamic, i.e., to activities.

Simultaneously, in the end of XIX century (1879) a new science formed - hydrogeology, which identifies ground waters as the object of professional attention. Among the problems solved by this science is also the issue of ground water composition and properties. Severe epidemics associated with water-supply (epidemics of the enteric fever in Paris) directed attention in the 1890s to ground water contamination. A result of this was a first service for the sanitary protection of water-supply sources in Paris.

Initially, ground waters were studied within the framework of geochemistry as one of geologic objects. Geochemists soon switched from comparing the composition of individual minerals to comparing composition of rocks, their associations and even entire geospheres. Such comparisons required an assiduous statistical analysis of the distribution of individual chemical elements. An American chemist, Frank Wigglesworth Clarke (1847–1931), expended 40 years of his life dealing with this painstaking and very labor-intensive work. In 1908 he published a fundamental monograph, *The data of geochemistry*, where he included results of his calculations of the Earth crust average elemental composition as well as that of various rocks, ground water, etc. Subsequently these data were numerously fine-tuned by F.W. Clarke himself and by other geochemists. Alexander Yevgenyevich Fersman (1883–1945) proposed to call these average values of individual elements content "clarkes" in honor of F.W. Clarke. Study of the clarke values showed that the element distribution on Earth decreases with the increase of their atomic mass. Greater than over, it so turned out that the contents of isotopes with even sequential numbers were higher than with odd numbers. Subsequent spectral analysis studies of elemental composition in meteorites and star atmospheres showed that these features in Earth composition are common for the galactic cosmic bodies, and that they reflect primordial distribution of elements prescribed by their nuclear properties. Nevertheless, the establishment of geochemistry as a science is associated with the names of Vladimir Ivanovich Vernadsky (1863–1945), A.E. Fersman and Victor Moritz Goldschmidt (1888–1947) who were the first to use the achievements of chemistry and thermodynamics for the explanation of processes within Earth.



Vladimir Ivanovich Vernadsky (1863–1945)

In the spring of 1882 the Russian Geological Committee was formed, where the hydrogeological discipline was overseen by Nikolay Fedorovich Pogrebov (1860–1942), who discovered radon in the waters of lake Lopukhinka. It is reasonable to consider him as a first official Russian hydrogeologist. An American geologist, Chase Palmer (1856–1927), studied waters in oil fields and in 1911 proposed a first ground water classification by the salt composition. This classification was for a long time commonly used abroad and in our country. First systematic ground water and their composition study in Russia is associated with the names of agrologist Vassily Vasilyevich Dokuchayev (1846–1903) and his students. Early in the XXth century he created in Petrograd a chemical laboratory of Russia's Ministry of Agriculture. In 1914 Pavel Vladimirovich Ototsky (1866–1943) noted a regular change in the properties and composition of ground waters in the Russian territory. Chemist Nikolay Semenovich Kurnakov (1860–1941) was among the first who studied brines, muds and salt deposits in Russia, and who introduced the concept of "metamorphization factor," which in 1917 he took as a basis for the classification of salt lakes. The same year J. Rogers observed a change in the composition of waters in California oil fields with depth and made a conclusion about reduction of their sulfates to H_2S. In 1920 analysis of deep ground waters in the US oil fields acquired systematic nature. At the same time in Russia in Novocherkassk by the efforts of Pavel Alexandrovich Kashinsky (1868–1956), who may be considered founding father of the domestic hydrochemistry, and Oleg Alexandrovich Alekin (1908–1995), there was created a first Hydrochemical institute. The studies of this period have been summarized by V.I. Vernadsky in 1929, in the Russian mineralogical society, where he presented a report "On the classification and chemical composition of ground waters." In this report, for the first time, the general discipline was defined, which was named ***geochemistry of ground water*** or ***hydrochemistry***. In 1933–1936 three volumes of *A history of ground waters* were published, in which V.I. Vernadsky systematized and gave an account of whatever was accumulated by the 1930s on this subject. Works by V.I. Vernadsky facilitated the merging of desultory studies on the ground water composition into a single general channel of hydrochemistry.

In 1920 in Novocherkassk the first Hydrochemical institute in the world was created. In the first stage, the underground and surface waters were studied together. In 1938 the term "hydrogeochemistry" appeared, associated with a study of the composition of ground water only. In 1948 O.A. Alekin published a first textbook "General hydrochemistry," in which ground waters were reviewed separately.

In the first stage, the main attention in hydrochemistry was devoted to methods of chemical analysis, and identification of ground waters by the composition, their classification and distribution. Significant attention was allotted to the search and mapping of potable and especially mineral waters and to industrial exploitation of salt lakes. In 1930 at the IV^{th} hydrogeology health-resort conference, a general practitioner and balneologist Mikhail Georgiyevich Kurlov (1859–1932) proposed the formula for a brief and visual description of ground water chemical composition. In 1933 Nestor Ivanovich Tolstikhin (1896–1992) used cyclograms for picturing the ground water composition, which were common until now. In 1935 Mikhail Georgiyevich Valyashko (1907–1984) utilized the schematics of N.S. Kurnakov and proposed his own classification of lake waters by their salt composition. Improvements of ground water hydrochemical classification were performed by Sergey Alexandrovich Shchukarev (1893–1984), Nikolay Nikolayevich Slavyanov (1878–1958), Vladimir Alexeyevich Sulin (1896–1950), O.A. Alekin, A.M. Piper, Alexander Mikhaylovich Ovchinnikov (1904–1969), Otar Sergeyevich Dzikiya, Elena Evstafyevna Belyakova and many others. Currently, practical significance is maintained by M.G. Kurlov's formula, and V.A. Sulin's (1946) and O.A. Alekin's (1948) classifications. In common use abroad is a diagram proposed in 1944 by A.M. Piper, and the pattern presented by Henry A. Stiff in 1951.

Simultaneously, the studies on the distribution of different composition ground waters were published. Russian agrologists were especially interested in ground waters and their composition. In 1923 Vsevolod Sergeyevich Ilyin (1888–1930) proposed a zoning scheme of these waters by the composition. His studies laid the basis for regional hydrogeochemistry in Russia. In 1934–35 the first papers were published by Constantine Lukich Malyarov and V.A. Sulin devoted to waters of Russia's oil fields. Special attention was devoted to mineral waters and lakes. The papers by N.S. Kurakov, N.N. Slavyanov, Vasily Alexandrovich Alexandrov (1877–1956), Alexy Ivanovich Dzens-Litovsky (1892–1971), M.G. Valyashko and others played a great role in this. In 1947 a monograph was published by A.M. Ovchinnikov called *Mineral waters*.

Successes in analytical chemistry enabled substantial expansion of the concepts about composition of ground waters. In 1935–1936 Vasily Petrovich Savchenko (1904–1971) and Anatoly Lvovich Kozlov (1903–1980) noted a correlation between the content of dissolved helium and the age of ground water. This period ended with the appearance of study manuals on the geochemistry of ground waters. In 1949 Victor Alexandrovich Priklonsky (1899–1959) and Fedor Fedorovich Laptev published apparently the first work devoted to a study of ground water composition. In 1953 O.A. Alekin published the first textbook, *Foundations of hydrochemistry*. In 1958 Vera Sergeyevna Samarina (1916–2002) published (apparently) the first textbook in Russia on the ground water composition, *Hydrochemical testing of ground waters*. In the US a similar work by John D. Hem (1916 –1994), *Study and interpretation of ground water chemical parameters* was issued in 1959.

<u>In the second stage,</u> in mid-XXth century, the issues of ground water genesis and formation became greater than pressing. In 1944 Georgy Alexeyevich Maximovich (1904–1979) introduced the concept of "ground water facies," and in 1958 Gregory Nikolayevich Kamensky (1892–1959) turned their attention to genetic types of ground water. Abroad, the first "hydrochemical facies" was identified by William Back (1925–2008) in 1960.

A discussion emerged relatively genesis of the ground waters of different composition, in particular great depth brines. Participants in this discussion were M.G. Valyashko, Alexander Ilyich Perelman (1916–1998), Yefim Vasilyevich Posokhov, I.K. Zaytsev, Yevgeny Victorovich Pinneker (1926–2001), Alla Ivanovna Polivanova (? –1996), Login Nazaryevich Kapchenko (1936–2006) and others. By the end of the 1950s papers appeared devoted directly to biochemical and chemical processes in ground waters. During this period Stanislav Romanovich Kraynov (1928–2007) studied rare elements, Vladimir Mikhaylovich Shvets (b. 1929) - distribution of organic matter and Sergey Ivanovich Kuznetsov (1900 –1987) and Lyudmila Evstafyevna Kramarenko – the role of microorganisms in the formation of the ground water composition. In 1961 Horton B. Craig (1926–2003) established linear correlation between isotope composition of hydrogen and oxygen in meteoric waters and drew attention to isotope composition of ground water.

In solving problems of ground water genesis and formation of its composition, hydrogeochemists turned to the fundamentals of chemical thermodynamics and physical chemistry. A special role in this belongs to the work by Robert Minard Garrels (1916–1988), *Mineral equilibrium at low temperature and pressures*, published in 1960, and in Russia in 1962. His work, especially the monograph, *Solutions, minerals, equilibrium*, written together with Charles Louis Christ (1916–1980), facilitated broader application of the laws and techniques of thermodynamics in studies of ground water formation. Of great significance were the publications of Sergey Alexandrovich Brusilovsky (b. 1936) about migration forms of elements in ground waters and also of Harold S. Helgeson (1931–2007), Igor Konstantinovich Karpov (1932–2005) and Boris Nikolayevich Ryzhenko (b. 1935). In study of brines a great merit belongs to Kenneth Sanborn Pitzer (1914–1997), who proposed in 1973 his high-density brines model. His papers noticeably raised the level of ground water formation hydrochemical studies. They introduced thermodynamical and kinetic methods in studies of the water-rock system, having thereby created the background for hydrochemical modeling. This transition of qualitative analysis of water composition formation processes from empirical to quantitative is the main achievement of this period. It enabled the transition from a description of what was to a prediction of what will be with the ground water composition in specific conditions.

Simultaneously, the field of hydrochemical studies widened. Onland, due to successes in drilling technology, hydrogeochemists penetrated to a depth of 12 km. Studies of mineral and hydrothermal waters became much greater than active. A new discipline appeared in hydrogeochemistry, which studied ground waters of seas and the ocean. This discipline was initially associated with study of ocean-bottom hydrothermal "smokers" and later with the results of deep-water drilling. At the same time, the domain of studied elements and isotopes in ground water expanded. Hessel de Vries (1916–1959), Vassily Ivanovich Ferronsly (b. 1925), Vladimir Timofeyevich Dubinchuk (b. 1936), Vladimir Andreyevich Polyakov and others published papers about natural isotopes of various elements in ground waters.

The third stage in the evolution of hydrogeochemistry was associated with aggravation of the ecological situation in industrial countries. It began in 1980s and was manifested in the interest from hydrogeochemists to investigation of consequences of the anthropogenic ground waters contamination. Successes of hydrogeochemistry in this area were associated in Russia with the names of Valentine Mikhaylovich Goldberg (1934–1996), Faina Ivanovna Tyutyunova and S.R. Kraynov, and in the West with the names of Jean J. Fred, Ch. D. Rail, D.M. Mackay, J.A. Cherry and others.

At this stage a major attention was devoted to technogenic compounds, their penetration subsurface, and spread and interaction when dissolved in ground water with rocks. As a consequence, the domain of hydrochemistry issues of applied nature associated with the determination of not only the state of the medium, but also its changes in real time, noticeably expanded. Successes in computer technology and applied mathematics, which allowed solving the ecological problems, turned out very helpful. In connection with this, the significance of hydrogeochemical monitoring and mathematic modeling drastically increased.

The first hydrogeochemical mathematical model of dissolved substance transfer was proposed, most likely, by J. P. Bredehoeft in 1973. Soon thereafter L.F. Konikov developed a similar model but with inclusion of components' dispersion in the process of migration. In our country, modeling evolved by the efforts of I.K. Karpov, Yuri Vsevolodovich Shvarov, Valery Nikolayevich Ozyabkin (b. 1937), Mikhail Boleslavovich Bukata (1950–2010), Gennady Anatolyevich Solomin, Mikhail V. Mironenko, Marina Valentinovna Charykova (b. 1961) and others. Eventually hydrochemical mathematic modeling became, beside the hydrodynamic one, a most common instrument of the applied hydrogeochemistry.

Numerical hydrochemical modeling stimulated studies in kinetics of the slowest hydrogeochemical processes, in particular, in dissolving speed. Over a relatively brief period, by the efforts of Antonio Lasaga, L. Neil Plummer, E. Lennart Soberg, Victor Alexeyevich Alexeyev (b. 1946) and others, the dissolution velocities of numerous aluminosilicate minerals were researched.

In connection with depletion of reserves and contamination of potable waters, the issue of civil rights for the water became acutely important. A first solution of this problem in Russia became RF law, "On the protection of the natural environment," which was enacted in 1991. Article 85 of the law for the first time in Russia gave the legal determination of ***ecological crime*** as the behavior causing social danger. Objects of this crime became the natural environment and its most significative components, in particular, ground waters. In 1996 ecological crime became the institute of Special part of the Russian criminal law (RF Penal code, Ch. 26: Ecological crimes). Under the Article 250 of this code, "contamination, pollution, depletion of surface or ground water, sources of potable water-supply or other change in their natural properties, if these deeds caused substantial damage to the wildlife or vegetation, fish reserves, forestry or agriculture," are ecological crimes. The consequence of ecological crime is ***ecological liability***, which involves incarceration of up to five years. And in 2007 the ***RF Water Code*** (*ВК РФ*) was enacted, which is a codified regulatory act controlling relations in the sphere of water use in Russia. It includes the entire section (Articles 95, 103 and 104) dealing with the protection of ground water against contamination.

Currently hydrogeochemistry is a fully formed science with a huge army of experts – hydrogeochemists. It is possible to identify within its framework four major disciplines:

1. General Hydrogeochemistry includes these subjects: physicochemical processes in the conditions of geologic medium; their interaction with rocks, oils or subsurface gases as well as migration mobility; balance and circulation of their chemical elements; and formation of ground water composition. Currently working in this discipline, in the Russian Federation, are V.P. Zverev, Klara Yefimovna Pityeva (b. 1924), Alexander Nikolayevich Pavlov (b. 1933), and abroad, Patrick A. Domenik, Franklin V. Schwartz, James I. Driver, and others.
2. Regional hydrogeochemistry studies and maps the distribution and behavior mostly of ground waters of different composition as a result of their formation conditions. Within the framework of this discipline are studied processes of rock weathering, soil formation and ground water composition under the effect of exogenous factors in specific geologic conditions. The whole army of professional hydrogeologists takes part in the description of ground waters in

various geologic conditions and in making hydrogeochemistry maps. In the Russian Federation these are K.E. Pityeva, Vladimir Andreyevich Kiryukhin (1930–2011), Stepan Lvovich Shvartsev (b. 1936) and abroad, James I. Driver, Charles V. Fitter (b. 1941) and others.

3. Endogenous hydrogeochemistry analyzes the formation and evolution of the composition of mostly deep thermal ground waters onland and in the ocean. This discipline studies hydrochemistry and formation of mineral, industrial and thermal waters; formation waters of oil and gas basins; ore and hydrothermal solutions; and their role in formation of economic deposits. In his time V.I. Vernadsky noted the existence of vertical zoning in water composition. Initially, it was studied by Nikolay Klimentyevich Ignatovich (1899–1950), Fedor Alexandrovich Makarenko (1906–1984), Constantine Vasilyevich Filatov (1907–1960s), N.I. Tolstikhin, Ivan Kireyevich Zaytsev (1907–1991), and some others. Currently it is possible to identify two different disciplines in endogenous hydrogeochemistry: oil-gas and hydrothermal. The oil and gas discipline deals with the formation waters of oil and gas basins in an environment of elevated temperatures and pressures, and their part in the formation of oil and gas fields and sedimentary ore bodies. The hydrothermal discipline deals with the formation of ground water composition in conditions of very high temperatures and pressures, and their part in processes of metamorphism and formation of hydrothermal ore deposits.
4. Applied hydrogeochemistry is oriented to the solution of specific economic issues. These issues include:

   a. Search and appraisal of ground water as an economic deposit (potable, mineral, industrial, thermal and other);
   b. Protection and monitoring of ground water quality, especially their commercial development areas;
   c. Engineering evaluation of the interaction between ground water and various technological materials in order to assure the reliability of engineering facilities and underground communications;
   d. Search of ore and oil-gas fields by indirect hydrochemical indications in ground water composition.