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Physicochemical modeling of water-rock-gas interactions in Russia

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Abstract
This is a review of physicochemical modeling of water-rock systems that is done in Russia. The history of the problem is considered, a list of publications is given, and the main results are described. This review will be in particular useful for foreign researchers.

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1. Introduction

The advances of modern hydrogeochemistry are considerable in many scientific fields. One of them is not directly related to the work of Vernadsky and relies on the development of physicochemical modeling, which provides insight into many hydrogeochemical problems on a fundamentally new scientific level. We therefore briefly discuss this problem in this paper.

The physicochemical modeling of hydrogeochemical processes in the water-rock-gas system has become widely used in geochemistry, following the studies of Garrels on water-mineral equilibria [1, 2] and the use of Eh-pH diagrams [3]. The first computer program for the calculation of the equilibrium state in the water-rock system was created by Helgeson [4-6]. Its use in the USSR had long been hampered by the lack of appropriate computer techniques.

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Fritz [7] designed an algorithm to determine the equilibrium mineral assemblage and the composition of aqueous solution for a series of rock/water proportions (increase of R/W), i.e., the model of successive movement of a single portion of aqueous solution through n areas of the rock (stepwise reactor).

Fouillac et al., [8] proposed an algorithm for calculating the compositions of equilibrium mineral assemblages and aqueous solutions after interaction of w-th wave of aqueous solution with s-th portion of the rock; i.e., the interaction model later termed as “multiwave flow step-wise reactor” (MFSR).

2. Modeling in Russia

In Russia, the first program simulating the equilibrium state of the “water-rock” system was created by Karpov, Kiselev, and Letnikov [9, 10] at the Vinogradov Institute of Geochemistry in Irkutsk (SibGEOKhI SB RAS). A need for thermodynamic data was satisfied by Handbook of Thermodynamic Data for Geologists (Atomizdat, Moscow, 1971). It was such relevant that it was translated into English by the US Geological Survey [11]. The physicochemical modeling was used by Korzhinskii to investigate the theory of metasomatic zonation [12].

Of great importance for the progress of thermodynamic modeling in Russia was the development of the GIBBS program at the Geochemical Department of the Moscow State University [13]. This program was aimed at calculating the equilibrium state of a system of any complexity and was later transformed into the HCh package for simulating geochemical processes [14, 15].

Grichuk and colleagues [16] presented a comparative analysis of the described model reactors and applied it to investigate several chemical processes. Reviews [17, 18] presented theoretical principles and described algorithms applied to model the equilibrium state of the “water-rock” system. Later several codes were designed and several geochemical problems modeled in Russia: GEOCHEM and GEOCHEQ program packages by Mironenko et al [19-21], Char'ykova and Char'ykov [22]. Bukaty et al [23, 24]. Nowadays, in Russia and other countries, there are several dozens of program packages for IBM-compatible personal computers combined with digital databases of the thermodynamic properties of materials or equilibrium constants of reactions.

At present, several groups of Russian specialists deal with modeling the hydrogeochemical and hydrothermal processes primarily using the SELECTOR and HCh packages. The modified versions of the MFSR method were recently proposed by other Russian research teams [19–21, 23, 24].

The use of thermodynamic numerical modeling allowed one to shed light on many particular questions of hydrogeochemistry, hydrothermal and sedimentary mineral formation, geocology, volcanology, and to move closer to a solution of some fundamental geochemical problems.

Based on the original contribution of Char'ykova and Char'ykov [22], the collaborators of St. Petersburg University simulated salt accumulation in the basins of modern evaporite sedimentation, evaporite accumulation of brines, and oceanic water, Caspian, Black, Azov, and Aral seas, Sivash and Kara-Bogaz-Gol bays, Kuchuk and Tanatar lakes [22]. The HydroGeo program complex designed in the Tomsk Polytechnical University [23] integrated a program of filtration of aqueous solution through a rock and computation of the equilibrium state of the “water-rock” system etc [19, 24]. In programs [19, 22, 23], the activity coefficients were calculated using the Pitzer model.

Among most significant results obtained using SELECTOR software are the models of secondary gold enrichment (its dissolution, transportation, and deposition) in the supergene zone [25], bauxite formation during weathering [28], and the origination of the Krivoi Rog-type banded iron formations on the basis of empirical geological material and concepts of the chemical evolution of the ocean–atmosphere–crust system of the Earth [26]. Successful simulation of mineral zoning in the weathering zone was hindered by a shortage in thermodynamic data on natural micas [27].

The GIBBS, GBFLOW software and HCh software package were applied to develop the thermodynamic models of hydrothermal vein mineral formation [29], submarine hydrothermal systems
[30], and formation of chemical composition of natural waters [31]; in the last work, the dissolution rates
of rock-forming mineral were normalized to that of halite [31].

The present issue of Geochemistry International includes three works. The paper of Galimov and
colleagues [32] provides the simulation results of the chemical composition of the primary aqueous phase
(and atmosphere) of the Earth. These results are based on the conclusion of biologists that plasma
membrane (including protein molecules) cannot emerge in the environment where Na prevails over K (as
it is observed in the modern ocean and land waters).

The work of Krynov, Ryzhenko and Cherkasova [33] showed that the formation of continental waters
of the Earth is mainly controlled by the following physicochemical factors: the mass ratio of interacting
rock and water (R/W), openness of the “water-rock” system relative to CO$_2$ and O$_2$, petrochemical rock
type, and the content of volatiles in it, and the temperature–pressure of their existence. The numerical
values of these factors define all known geochemical types of natural water.

The petrochemical type of the rock affects the composition of aqueous phase via the dissolution rate of
rock minerals, especially volatile-bearing minerals. The decrease in water exchange and increase of R/W
($10^{-6}$ $\rightarrow$ $10^2$) is accompanied by the increase in salinity of aqueous phase, as well as in the fractions of Cl,
Na, Ca (in closed system) or HCO$_3$, Cl, Na (in system open with respect to CO$_2$). The contents of
extractable chlorine and reactive organic matter in the rock have the most significant effect on the
composition of aqueous phase, defining its geochemical type.

The closure of the “water-rock” system leads to the formation of calcium–chloride aqueous phase,
while sodium–carbonate waters are formed in the “water-rock” system open with respect to CO$_2$. An
increase in temperature shifts the acid-basic state of aqueous phase in the alkaline field, while that of the
redox state, in the reduced field.

Finally, the studies of Grichuk [34] are dedicated to one of the most debatable geochemical problems
of hydrothermal process: the role of magmatic fluids in the hydrothermal ore formation. This question is
considered by the urgent example of modern submarine hydrothermal vents in island arcs.

References

[1] Garrels RM. Mineral equilibria Addison-Wesley Readings ;1959.
[2] Garrels RM and Christ CL. Minerals, solutions and equilibria New York: Harper and Rowlay; 1965.
[3] Brookins DG. Eh-pH diagrams for geochemistry Berlin: Springer-Verlag; 1988.
[4] Helgeson HC. Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions. I.
Thermodynamic relations. Geochem Cosmochim Acta 1968; 32: 853–877.
[5] Helgeson HC, Garrels RM, MacKenzie FT. Evaluation of irreversible reactions in geochemical processes involving minerals and
aqueous solutions. II. Applications. Geochem Cosmochim Acta 1969; 33: 455–481.
[6] Helgeson HC. Mass transfer among minerals and hydrothermal solutions,” in Geochemistry of hydrothermal ore deposits, 2nd
Edition, Ed by H. L. Barnes New York: John Wiley & Sons; 1976.
[7] Fritz B. Etude Thermodynamique et simulation des réactions mineraux - solutions. Application à la géochemie des alterations Et
des eaux continentales, Memoire des Sciences Geologiques. Strasbourg. 1975; No. 11.
[8] Fouillac C, Michard G, Boequier G. Une méthode de simulation de l’évolution des profiles d’alteration. Geochem Cosmochim
Acta 1977; 41: 207–213
[9] Karpov IK, Kiselev AI, Letnikov FA. Chemical thermodynamics in petrology and geochemistry. Irkutsk; 1971 [in Russian].
[10] Karpov IK, Kiselev AI, Letnikov FA. Computer modeling of natural mineral formation. Moscow; Nedra: 1976 [in Russian].
[11] Naumov GB, Ryzhenko BN, Khodakovskii IL. Handbook of thermodynamic data. Springfield: 1974.
[12] Korzhinskii DS. Theory of metasomatic zoning. Moscow : Nauka; 1969 [in Russian].
[13] Shvarov YuV, Calculation of equilibrium state in the multicomponent heterogenous system. Dokl USSR AS 1976; 229: 1224–
1226.
[14] Shvarov YuV. Algorithmization of the numeric equilibrium modeling of dynamic geochemical processes. *Geochem Int* 1999; 37:562–570.

[15] Shvarov YuV. HCh: New potentialities for the thermodynamic simulation of geochemical systems offered by Windows. *Geochem Int* 2008; 46: 834–839.

[16] Grichuk DV, Shvarov YuV. Comparative analysis of techniques used in the equilibrium-dynamic simulations of infiltration metasomatic zoning. *Petrology* 2002; 10: 580–592.

[17] Mironenko MV, Bukaty MB. Computer modeling of physicochemical processes in the water–rock system in *Geological evolution and self-organization of the water–rock system. Vol. 1. Water–Rock System in the Earth’s Crust: Interaction, Kinetics, Equilibrium, and Modeling.* Novosibirsk: Nauka; 2005; 171–220 [in Russian].

[18] Chudnenko KV. *Thermodynamic modeling in geochemistry: theory. Algorithms, Softwares, and Applications.* Novosibirsk: GEO; 2010 [in Russian].

[19] Mironenko MV, Akinfiev NN, Melikhova TYu. GEOCHEQ–Complex for thermodynamic modeling of geochemical systems. *Vestn. OGGGM Ross. Akad Nauk* 2000; 2: 96–97.

[20] Mironenko MV, Zolotov MYu. Equilibrium–kinetic model of water–rock interaction. *Geochem Int* 2012; 50: 1–7.

[21] Silantyev SA, Mironenko MV, Novoselov AA. Hydrothermal systems in peridotites of slow-spreading mid-oceanic ridges. Modeling phase transitions and material balance: Downwelling limb of a hydrothermal circulation cell. *Petrology* 2009; 17: 138–157

[22] Charykova MV, Charykov NA. *Thermodynamic modeling of evaporite sedimentation.* St. Petersburg: Nauka; 2003 [in Russian].

[23] Bukaty MB. Problems of numerical modeling of geomigration In: *Groundwaters of the east Tyumen: Tyumenskii Dom Pechati.* 2009; 413–416.

[24] Lukin AA, Bukaty MB, Lukin AlAn, Shmurygina EV, Zubkov AA, Danilov VV. Water balance estimate of safety of liquid radioactive waste disposal in *Groundwaters of the east Tyumen: Tyumenskii Dom Pechati.* 2009; 395–398

[25] Diman EN, Karpov IK, Makarov VN. *Computer modeling of supergene processes.* Moscow: Nauka; 1982 [in Russian].

[26] Drozdovskaya AA. *Chemical evolution of the ocean and atmosphere in the geological history of the earth.* Kiev: Naukova dumka; 1990 [in Russian].

[27] Kopeikin VA. Physicochemical model of laterite process In: *Physicochemical models in geochemistry.* Novosibirsk: Nauka; 1988: 61–80 [in Russian].

[28] Kashik SA. *Formation of mineral zoning in the weathering zones.* Novosibirsk: Nauka; 1989 [in Russian].

[29] Borisov MV. *Geochemical and thermodynamic models of veined hydrothermal mineral formation.* Moscow: Nauchnyi mir; 2000 [in Russian].

[30] Grichuk DV. *Thermodynamic models of submarine hydrothermal processes.* Moscow: Nauchnyi mir; 2000 [in Russian].

[31] Krainov SR, Ryzhenko BN, Shvets VM. *Geochemistry of groundwaters. Theoretical, applied and ecological Aspects* Moscow: Nauka; 2004 [in Russian].

[32] Galimov EM, Natochin Yu.V, Ryzhenko BN, Cherkasova EV. Chemical composition of the primary aqueous phase and origin of life. *Geochemistry Intern* 2012; 50-N13: 1048-1068.

[33] Ryzhenko BN, Cherkasova EV. Chemical composition of natural waters and brines as a result of hydrochemical processes in water-rock-gas systems. *Geochemistry Int* 2012; 50-N13: 1101-1150.

[34] Grychuk DV. Thermodynamic model of ore formation in marine hydrothermal system. *Geochemistry Int* 2012; 50-N13: 1069-1100.