Lithological and Hydrogeochemical Implications of Ion Exchange in Sedimentary Basins: Evidence from the Volga–Ural Basin

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Abstract—Implications of ion exchange processes for the formation of lithological and hydrogeochemical systems under various thermobaric conditions of the subsurface hydrosphere are discussed on the basis of on-location, experimental, and thermodynamic studies. It is shown for the case of the Volga–Ural sedimentary basin that ion exchange interaction in the water–rock system bears a zonal character and is differentiated with depth. Exchange and adsorption processes are most efficient in the upper 500-m-thick supergene zone composed of terrigenous clayey rocks, where the HCO$_3^-$–Na- and SO$_4^{2-}$–Na-waters with a mineralization reaching 20 g/dm$^3$ are formed. In cata- and metagenetic zones at a depth of more than 1000–1500 m, these processes do not strongly affect the brine composition. Metasomatic dolomitization of limestones as an exchange adsorption process plays the crucial role in the formation of Cl–Ca-brines at that depth.

PRINCIPLES AND KINETICS

OF MASS EXCHANGE

Epigenetic transformation of groundwater and sedimentary rocks by ion exchange is among the problems that equally pertain to hydrogeochemistry and lithology. Various aspects of this problem were discussed by A.N. Buneev, K.K. Gedroits, E.G. Degens, J. Driver, A.B. Ronov, E.M. Sergeyev, N.M. Strakhov, V.N. Kholodov, V.M. Shvets, S.R. Krainov, and other Russian and foreign researchers. Processes of ion exchange include exchange adsorption and exchange absorption interactions in lithological and hydrogeochemical systems of sedimentary basins that combine absorption and reproduction of dissolved matter. Exchange adsorption is mostly a surface phenomenon, whereas the exchange absorption proceeds within the entire solid phase body; i.e., it affects not only the surface of mineral particles, but also the internal structure (lattice of rock-forming minerals).

Kinetics and lithological–hydrogeochemical implications of ion exchange between solid and liquid phases in sedimentary basins are controlled by hydrogeodynamic and thermobaric conditions varying with depth. As a result, both ion exchange processes and resultant geochemical types of groundwater bear a zonal character.

The mechanism of exchange adsorption consists in equivalent stoichiometric replacement of ions in the double electric layer of clay minerals by ions of the free solution (as a result, ions of clay minerals transfer into the solution). The absorption energy (adsorption capacity) of ions and their concentration in solution and absorbed complex (AC) of rocks are the main factors controlling the intensity and direction of exchange adsorption processes. As was experimentally established (Aborenko, 1985; Gedroits, 1975), the adsorption capacity of cations falls with decrease of their valence and reduction of atomic radius for equally charged ions. Hydrogen ion is the only exception, because its adsorption activity is higher than the activity of not only one-valent, but also two- and three-valent cations: $\text{H}^+ > \text{Al}^{3+} > \text{Fe}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$.

Highly dispersed rocks (grain size <0.001 mm) have the highest adsorption capacity. Therefore, exchange adsorption processes demonstrate the highest hydrogeochemical effect in porous terrigenous (significantly clayey) rocks with AC as the main repository of exchange cations. The ability of clay minerals to exchange ions with solutions is governed by two principal compositional and structural factors, namely specific surface and crystal chemistry of basal surfaces (Sergeev et al., 1971).

Aluminosilicates of chlorite, halloysite, and kaolinite (including nacrite and daccite) groups have a rigid lattice of 1:1 type with a small interlayer space (~0.7 nm) that prevents from emplacement of hydrated cations into the interpacket space of their structure. As a result, they do not participate in ion exchange. Basal surfaces are also subordinate in this process. The main mass of exchange cations is localized on lateral sides of the lattice serving as the main area for adsorption. The phenomenon of isomorphic replacement, which creates uncompensated electric charges, is atypical for miner-
als of the kaolinite group. Their specific surface accessible for interaction with solution is 8–20 m$^2$/g, and their AC capacity is 3–15 mmol/100 g.

In contrast to kaolinite, the three-layer (2:1) clay minerals of smectite group (montmorillonite, bentonite, beidellite, nontronite, sauconite, and saponite) have a mobile lattice with the interlayer space reaching 15–20 nm. Owing to this feature and the presence of uncompensated charges in the structure of minerals of the smectite group as a result of the heterovalent isomorphism ($\text{Si}^{4+} \rightarrow \text{Al}^{3+}$ in tetrahedral sheets and $\text{Al}^{3+} \rightarrow \text{Mg}^{2+}$, $\text{Al}^{3+} \rightarrow \text{Fe}^{2+}$ in octahedral sheets), the cation sorption from solutions proceeds not only on lateral sides and basal surfaces, but also within the interlayer space containing the main mass of adsorbed ions (up to 80%). The specific surface of smectite minerals attains an enormous value of 600–800 m$^2$/g, and their AC capacity is 150–200 mmol/100 g.

In terms of exchange adsorption properties, hydromicas occupy a transitional position between minerals of the kaolinite and smectite groups. Their specific surface and AC capacity are equal to 30–180 m$^2$/g and 10–40 mmol/100 g, respectively. Hydromicas have expanding crystalline lattices of 2:1 type that inhibit the penetration of water molecules. Heterovalent replacements are widely developed in hydromicas. Therefore, their lateral sides acquire a negative charge. Therefore, the broken bonds at crystal margins and their outer basal surfaces serve as active surfaces of hydromicas. Therefore, hydromicas capable to the ion exchange interaction with water.

The composition of ions absorbed by sedimentary rocks is primarily determined by the cation composition of water in sedimentary basin. Two main (marine and continental) AC types are recognized in this respect. Sodium and potassium are predominant in the first type ($\text{rNa} + \text{rK} > \text{rCa}$), while calcium prevails in the second type ($\text{rCa} > \text{rNa} + \text{rK}$). The variation of hydrochemical regime of sedimentation and the emplacement of genetically alien infiltration (metageneic) water into sedimentary rocks saturated with sedimentation (thalassogenic) water generally give rise to the AC saturation with cations having a high absorption energy ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$) and the gain of ions with a lower adsorption activity ($\text{Na}^+$, $\text{K}^+$) in solution.

Exchange adsorption is the most rapid hydrogeochemical process in the water–terrigenous rock system. In suspension, equilibrium between cations of AC and solution is attained in a very short time span measured by minutes (Gedroits, 1975; Popov et al., 1992). Therefore, the geological time factor can be ignored in the estimation of hydrogeochemical significance of ion exchange between solid and liquid phases in various hydrodynamic environments of the lithospheric sedimentary layer.

Under natural conditions, kinetics of exchange adsorption is significantly controlled by convective–diffusive transfer of the dissolved material to the ion exchange surface and removal of reaction products from the lithological–hydrogeochemical systems, i.e., by the hydrodynamic situation in the interaction zone of solid and liquid components. Thus, disequilibrium character of the system is maintained due to the cation concentration gradients within the solution, as well as between the solution and double electric layer of clay minerals. This implies that hydrodynamically mobile supergene zones, which are open for material and energy exchange with the environment, are most favorable for exchange adsorption in clay rocks and metamorphism of groundwater therein.

The AC capacity of clay minerals depends not only on their crystal chemistry, but also on acid–alkaline and $PT$ conditions of subsurface hydrosphere. As a rule, the AC capacity of sedimentary rocks steadily decreases with increase in $T$, $P$, and depth. This is accompanied by decrease in pH of groundwater and compaction and lithification of rocks.

The mass of cations, which may potentially be supplied from AC into groundwater, is eventually controlled by the AC capacity and porosity of terrigenous rocks. The influence of solid phase capacity on groundwater composition is evident. The quantitative contribution of porosity ($n$) to groundwater metamorphism is not so obvious, because the increasing dispersibility of sedimentary rocks simultaneously leads to the growth of both AC capacity and $n$. Therefore, the AC capacity in the sand–silt–clay series increases from 5 to 100 mmol/100 g, whereas $n$ increases from 20 to 80%.

Let us take two end members of this series and infer that the complete cation exchange with the removal of all adsorbed ions into solution occurs in a water-saturated sand with AC capacity $C_1 = 20$ mmol/100 g and porosity $n_1 = 25\%$ and in clay with AC capacity $C_2 = 100$ mmol/100 g and porosity $n_2 = 70\%$. If the sand density is $\rho_1 = 2.65$ g/cm$^3$ and the clay density is $\rho_2 = 2.75$ g/cm$^3$, the total volume of 100 g of rock (including pores) is $V_1 = 50.3$ cm$^3$ in the first case and $V_2 = 121.2$ cm$^3$ in the second case. The pore volume equals $V'_{1} = 12.6$ cm$^3$ and $V'_{2} = 84.9$ cm$^3$, respectively. Hence, the maximum amount of adsorbed ions that may be supplied to the pore solution from AC is $C'_1 = 20$ mmol/12.6 cm$^3$ for sand and $C'_2 = 100$ mmol/84.9 cm$^3$ for clay (or $C'_1 = 1587$ mmol/dm$^3$ and $C'_2 = 1179$ mmol/dm$^3$ of solution). This amount of adsorbed ions in solution will be provided by the sand mass $m_1 = 7.9$ kg and the clay mass $m_2 = 1.2$ kg.

As can be seen, the metamorphising effect of exchange adsorption in sand is higher than in clay, although the AC capacity of clay is five times higher than that of sand.

The role of ion exchange in metamorphism of the cation composition of water in rocks with the same AC capacity but different $n$ values can be illustrated by the...