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–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. Sergeev, 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: $H^+ > Al^{3+} > Fe^{3+} > Mg^{2+} > Ca^{2+} > Na^+ > K^+ > NH_4^+$.

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 m²/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 ($Si^{4+} \longrightarrow Al^{3+}$ in tetrahedral sheets and $Al^{3+} \longrightarrow Mg^{2+}$, $Al^{3+} \longrightarrow Fe^{2+}$ 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 m²/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 m²/g and 10–40 mmol/100 g, respectively. Hydromicas have unexpanding 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 hydromicaceous minerals 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 (rNa + rK > rCa), while calcium prevails in the second type (rCa > rNa + rK). The variation of hydrochemical regime of sedimentation and the emplacement of genetically alien infiltration (meteogenic) water into sedimentary rocks saturated with sedimentation (thalassogenic) water generally give rise to the AC saturation with cations having a high absorption energy (Ca^{2+}, Mg^{2+}) and the gain of ions with a lower adsorption activity (Na^+, 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/cm³ and the clay density is $\rho_2 = 2.75$ g/cm³, the total volume of 100 g of rock (including pores) is $V_1 = 50.3$ cm³ in the first case and $V_2 = 121.2$ cm³ in the second case. The pore volume equals $V_1' = 12.6$ cm³ and $V_2' = 84.9$ cm³, 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 cm³ for sand and $C_2' = 100$ mmol/84.9 cm³ for clay (or $C_1' = 1587$ mmol/dm³ and $C_2' = 1179$ mmol/dm³ 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.
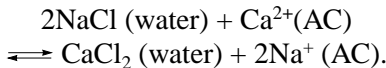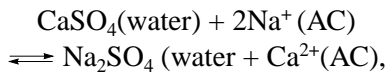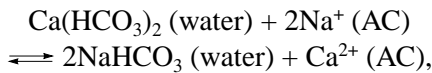
The role of ion exchange in metamorphism of the cation composition of water in rocks with the same AC capacity but different n values can be illustrated by the

following example. Assume that C_1 and ρ_1 of sand are the same as in the first case, but their n value varies by 25–50%. As was shown, the mass of adsorbed ions in solution at $n_1 = 25\%$ is 1587 mmol/dm^3. If the sand porosity increases to $n_2 = 50\%$, then the amount of cations removed from AC drops to 530 mmol/dm^3.

The results obtained indicate that the rock porosity may be a more significant factor of metamorphism of water composition than the AC capacity. In any case, the increase in water-saturated pore volume at the constant AC capacity inevitably should diminish the mass of adsorbed ions supplied to the solution.

Under realistic lithological–hydrogeochemical conditions of the crustal sedimentary cover ($n = 5$–70%, AC capacity = 1–100 mmol/100 g, and water mineralization $M < 500$ g/dm^3), the mass of adsorbed ions in groundwater may vary in a wide range from a few tens to thousands of mmol/dm^3. The ion exchange capacity of sedimentary rocks with various n values based on empirical data is shown in Fig. 1.

Reactions of ion exchange adsorption are most often used to interpret sodic, sodium sulfate, and calcium chloride waters that cannot generally be formed by a direct extraction of the respective salts because of their extremely low abundance in sedimentary rocks:

$$Ca(HCO_3)_2 \text{ (water)} + 2Na^+ \text{ (AC)}$$
$$\rightleftharpoons 2NaHCO_3 \text{ (water)} + Ca^{2+} \text{ (AC)},$$

$$CaSO_4 \text{(water)} + 2Na^+ \text{ (AC)}$$
$$\rightleftharpoons Na_2SO_4 \text{ (water} + Ca^{2+}\text{(AC)},$$

$$2NaCl \text{ (water)} + Ca^{2+}\text{(AC)}$$
$$\rightleftharpoons CaCl_2 \text{ (water)} + 2Na^+ \text{ (AC)}.$$

The above processes are reversible. However, in terms of power consumption, reactions from the left to right are most efficient in the first and second cases, but from the right to left in the third case (Lebedev, 1965). Owing to the higher Ca^{2+} absorption energy in comparison with Na^+, the resultant lithological and hydrogeochemical systems are most stable under natural conditions.

In contrast to the exchange adsorption, the exchange absorption proceeds under high PT conditions and consists in the metasomatic and isomorphic replacement of large cations in rocks by cations from water (brine) with smaller ionic radii. During the interaction of terrigenous aluminosilicate and carbonate rocks with Cl–Na–Mg-brines, Ca^{2+} passes into solution with the formation of Cl–Ca-brines and drastic change in the mineral composition of rocks themselves:
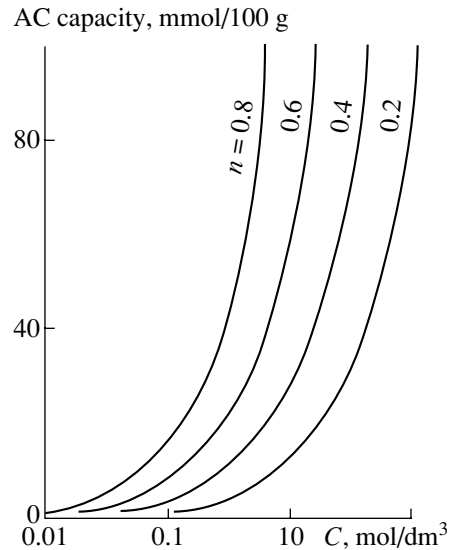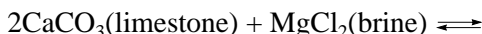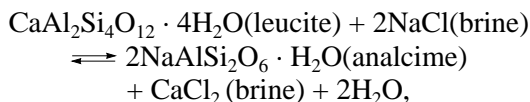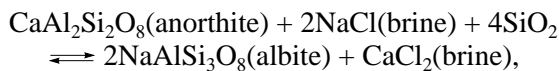
$$CaAl_2Si_2O_8\text{(anorthite)} + 2NaCl\text{(brine)} + 4SiO_2$$
$$\rightleftharpoons 2NaAlSi_3O_8\text{(albite)} + CaCl_2\text{(brine)},$$

$$CaAl_2Si_4O_{12} \cdot 4H_2O\text{(leucite)} + 2NaCl\text{(brine)}$$
$$\rightleftharpoons 2NaAlSi_2O_6 \cdot H_2O\text{(analcime)}$$
$$+ CaCl_2 \text{ (brine)} + 2H_2O,$$

$$2CaCO_3\text{(limestone)} + MgCl_2\text{(brine)} \rightleftharpoons$$

AC capacity, mmol/100 g

Fig. 1. Amount of adsorbed ions (C) in solution vs. AC capacity and porosity (n) of rock.

$$CaCO_3 \cdot MgCO_3\text{(dolomite)} + CaCl_2\text{(brine)}.$$

Since the ionic radius of Ca^{2+} (0.104 nm) removed from crystalline lattices of aluminosilicates and carbonates is higher than that of Na^+ (0.098 nm), Mg^{2+} (0.074 nm), and Si^{4+} (0.039 nm) in solution, the above reactions proceeding from left to right are generally efficient. It is noteworthy that the mineralization of metamorphosed brines is variable due to the equivalent character of the interphase reactions and different masses of ions Na^+ (22.99) and Mg^{2+} (12.16), on the one hand, and Ca^{2+} (20.04), on the other. The Mg^{2+}–Ca^{2+} exchange results in the increase of mineralization from 450 to 640 g/dm^3. The Cl–Ca brines with such a high degree of mineralization were detected in Lower Paleozoic rocks of the Siberian and North African platforms.

Highly mineralized Cl–Na–Mg- and Cl–Mg-brines, which are products of the condensation of mother halogenic brines in evaporite basins prior to the final halite, carnallite, and bischofite stages of halogenesis, participate in reactions producing albite, analcime, and dolomite. Based on experimental and field experiments, the Mg^{2+} concentration decreases from 120–80 to 5–1 g/dm^3, while the Ca^{2+} concentration grows from 0.1–2.4 to 60 g/dm^3 or more during the transformation of Cl–Mg-brines into Cl–Ca-solutions.

The character of exchange absorption is primarily controlled by facies conditions of sedimentation and evolution of hydrogeological structures. The presence of saliferous sequences and paragenetically associated Cl–Na- and Cl–Mg-brines in the sedimentary cover is a necessary condition for the development of exchange absorption. Metamorphism of Mg-brines by the reaction of dolomitization is typical of basins filled with carbonate and terrigenous–carbonate rocks.

Basins of this kind are widespread in the ancient (epi-Karelian) East European and Siberian platforms (Pripyat and Cisural troughs, Caspian and Buzuluk basins, Irkutsk Amphitheater, and others). Paleozoic carbonate rocks and evaporites in these troughs and basins vary in age from Early Cambrian to Late Permian. The largest evaporite water reservoirs as sources of Cl–Mg-brines existed in the Early Cambrian (eastern Siberia), Middle–Late Devonian (Dnieper–Donets Basin), and Early Permian (Volga–Ural region). Penetration of highly mineralized ($M = 320$–510 g/dm^3) and heavy ($\rho = 1.227$–1.367 g/cm^3) brines into underlying carbonate rocks was driven by the mechanism of density (concentration) convection (Popov, 2000).

Under natural conditions, processes of metasomatic dolomitization of limestones are realized in the geological time scale, because they proceed according to the intradiffusion mechanism. Therefore, it is not accidental that the rCa/rMg value in sedimentogenic brines has commonly a direct correlation with the duration of their interaction with carbonate rocks. This ratio varies from 0.2 in the present-day brines to 1.3 in Mesozoic brines and 10 or more in Paleozoic brines (Panchenko, 1966).

It should be emphasized that the replacement of Mg^{2+} of brine by Ca^{2+} of solid phase, which leads to the gain of Ca^{2+} in Cl-brine, is also reproduced in experiments (Vlasova and Valyashko, 1969). The Cl–Na–Mg-brines corresponding to different stages of halogenesis were used as a liquid phase, while $CaCO_3$ was used as a solid phase. The experiments were carried out in autoclaves at $T_1 = 150°C$, $T_2 = 200°C$, and $P \leq 60$ MPa with an exposition period of 7 days. All runs demonstrated an enrichment of solution in Ca^{2+} ions and depletion in Mg^{2+}. Under different combinations of hydrogeochemical and thermobaric parameters, insignificantly the amount of Na^+ ions in the final solutions decreased or increased. Calcite ($CaCO_3$) and magnesite ($MgCO_3$) were the prevalent solid phases at 150°C, whereas dolomite ($CaCO_3 \cdot MgCO_3$) was predominant at 200°C. The influence of pressure on dolomite formation was not established. It entirely depends on M, Mg^{2+} concentration in solution, rCa/rMg value, and T.

It should also be noted that due to the equivalent character of interphase reactions and different molar volumes of calcite and dolomite, dolomitization markedly increases porosity (by 10–12%) and, in particular, permeability (by several orders of magnitude) of the primary carbonate rocks.

In addition to the above-mentioned factors, the intensity and lithological–hydrogeochemical consequences of the exchange absorption in limestones substantially depend on the character of their pore space. In porous and porous–cavernous carbonate sediments, the influence of secondary dolomitization on the mineral composition of sediments and the ion–salt composition of groundwaters will be much greater than in rocks with fissure-type porosity. This statement is supported by results of regional lithological–hydrogeochemical studies. For example, in the Cisural region characterized by an areal penetration of Permian Cl–Mg-brines into underlying Carboniferous carbonate rocks, the rCa/rMg ratio of Cl–Ca-brines is 5–20. In the Pripyat Trough, the Devonian halogenic brine was locally delivered from the Lebedyan Basin to underlying Zadonsk–Yelets limestones along tectonic faults and fractures (Poroshin, 1981). The rCa/rMg value in subsalt brines is commonly ≤ 5.

HYDROGEOCHEMICAL ZONING OF SEDIMENTARY BASINS

The vertical (deep) hydrogeochemical zoning is a principal attribute of groundwater in the Earth's interior. In sedimentary basins of the platform type, the zoning is mainly governed by the composition of sequences of the sedimentary cover and hydrodynamic conditions. Regional hydrogeological studies showed that the sedimentary section penetrated deep boreholes (up to 5–7 km) is dominated by the direct hydrogeochemical zoning, i.e., increase in the M value of groundwaters with depth due to the involvement of more and more soluble salts.

This paper presents results of the investigation in the Volga–Ural sedimentary basin, one of the largest sedimentary structures in the East European Platform. This basin is characterized by an extreme diversity of hydrogeochemical and lithofacies conditions. The sedimentary cover consists of Upper Proterozoic and Phanerozoic rocks. However, Paleozoic (Devonian, Carboniferous, and Permian) largely marine carbonate rocks, up to 2–3 or more km thick, are most abundant. Evaporites (dolomite, gypsum, sodium and potassium salts) as indicators of ancient brine reservoirs occupy a considerable (up to 500 m and more) portion of the Lower Permian (Kungurian) section. The gypsum–dolomite facies are known in Frasnian and Famennian stages (Upper Devonian), Visean and Moscovian stages (Middle Carboniferous), and Gzhelian Stage (Upper Carboniferous). Upper Permian polyfacies (coastal-marine, lagoonal, and continental) sequences are substantially terrigenous and clayey. Terrigenous, largely continental sediments also sporadically occur at various Carboniferous and Devonian stratigraphic levels.

The Kungurian saliferous sequence divides the sedimentary cover of the basin into two hydrogeochemical stages. The upper stage is composed of five zones of oxygen- and nitrogen-rich infiltration waters (from top to bottom): (1) calcium hydrocarbonate (HCO_3–Ca) zone with $M = 0.3$–1.0 g/dm^3, (2) sodium hydrocarbonate (HCO_3–Na) zone with $M = 0.5$–1.2 g/dm^3, (3) calcium sulfate (SO_4–Ca) zone with $M = 1$–3 g/dm^3, (4) sodium sulfate (SO_4–Na) zone with $M = 1.5$–20 g/dm^3, and (5) calcium and sodium sulfate–chloride (SO_4–Cl–Ca–Na) zone with $M = 5$–40 g/dm^3.

The Kungurian sequence encloses methane- and nitrogen-rich sodium–magnesium chloride (Cl–Na–Mg) brines with $M = 230–470$ g/dm^3 (zone 6). It is locally developed within the Solikamsk, Buzuluk, and Caspian basins.

In the lower, sub-Kungurian stage, the hydrogeochemical section is supplemented by the following zones: (7) sodium chloride (Cl–Na) zone with hydrogene sulfide, carbon dioxide, nitrogen, and methane ($M = 36–320$ g/dm^3) and (8) sodium and calcium chloride (Cl–Na–Ca) zone with hydrogen–methane or only methane ($M = 200–330$ g/dm^3 or more).

The increase in mineralization and change of gas-water composition with depth is accompanied by increase in temperature (up to 50°C or more) and pressure (up to 30 MPa or more) but decrease in the redox and acid-alkaline potential of water (Eh from +650 to −450 mV, pH from 8.8 to 5.0).

The water-bearing rocks also undergo substantial epinenetic alterations with depth. In terrigenous sediments, clay minerals of the smectite group, which are typical of the upper supergene zone (<500 m), gradually give way to hydromica, kaolinite, and chlorite that prevail in cata- and metagenetic zones at a depth greater than 1.5–2.0 km. Metasomatic processes providing the formation of epigenetic dolomites play a significant lithological and hydrogeochemical role in carbonate rocks.

Turning again to hydrogeochemical zoning, it should be noted that processes of ion exchange are not involved in the formation of HCO$_3$–Ca, SO$_4$–Ca, Cl–Na-, and SO$_4$–Cl–Ca–Na-waters. Their formation is controlled by the dissolution and extraction of carbonates, gypsum, and halite with the participation of biochemical processes, hydrolysis of aluminosilicates, and water mixing. The molecular diffusion of Na$^+$ and Cl$^-$ from salts also takes part in the formation of subsalt and suprasalt Cl–Na-brines.

Intrasalt Cl–Na–Mg-brines make up slightly altered mother brines of the Kungur halogenic basin at the halite–carnallite stage of halogenesis. These syngenetic (relative to the host salt) relict brines were developed at the regional scale during the origination and evolution of the Early Permian halogenic basin (Popov, 2000).

As concerns the HCO$_3$–Na- and SO$_4$–Na-waters and economic Cl–Na–Ca-brines as valuable mineral deposits, their nature remains rather ambiguous and can be interpreted in different ways. Analysis of existing concepts on the genesis of these waters shows that neither extraction of readily soluble salts, nor mixing processes and biochemical sulfate reduction cannot lead to their formation. Their origin in the Volga–Ural Basin was not discussed in terms of ion exchange, because the respective evidence was lacking. In order to provide insights into this problem, more than 400 AC samples from Upper Proterozoic, Paleozoic, and Cenozoic terrigenous rocks were analyzed in combination with petrographic, thermal, and XRD studies, experimental
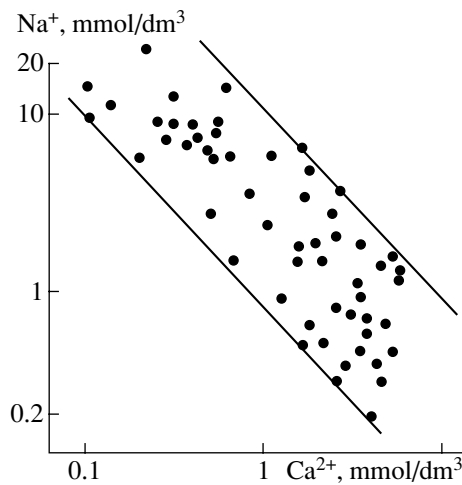

Fig. 2. Correlation between Na$^+$ and Ca^{2+} concentrations in carbonated water.

works, and lithological and hydrogeochemical balance calculations for the water–rock system.

HYDROGEOCHEMISTRY OF EXCHANGE ADSORPTION

As was mentioned above, zones of HCO$_3$–Na- and SO$_4$–Na-waters pertain to the upper stage of the Volga–Ural Basin composed of Upper Permian terrigenous, mainly quartz–feldspathic rocks. The feldspar content in sandstones, which serve as the major aquifers, amounts to 5–15%. The feldspars are mainly represented by plagioclase (andesine and oligoclase), i.e., Ca–Na-aluminosilicates.

The HCO$_3$–Na-waters ($M = 0.5–1.2$ g/dm^3) are confined to the boundary units of zones with free and difficult water exchange. These waters occur at a depth of 50–200 m within a 60- to 80-m-thick zone. The soda (NaHCO$_3$ + Na$_2$CO$_3$) content in the salt composition attains 1100 mg/dm^3 (92%). This is a purely alkaline solution with pH = 7.3–8.6 and Eh varying from 100 to 300 mV ($T = 4–6$°C).

The hydrolytic and exchange adsorption concepts of HCO$_3$–Na-water formation in terrigenous rocks may be regarded as competitive hypotheses. According to (Shvartsev, 1982), the gain of Na$_2$CO$_3$ during aluminosilicate hydrolysis (carbon dioxide weathering) starts with CaCO$_3$ saturation. This conclusion is based on different solubilities of CaCO$_3$ and Na$_2$CO$_3$. However, it turned out that with increase in mineralization from 0.3 to 1.2 g/dm^3, the Na$^+$ concentration steadily grows up, whereas the Ca^{2+} concentration diminishes. In the most mineralized sodic water, the Ca(HCO$_3$)$_2$ content varies from <40 to 10 mg/dm^3, whereas the CaCO$_3$ solubility attains 500 mg/dm^3 even at a low CO$_2$ concentration (<50 mg/dm^3). The inverse correlation between Na$^+$ and Ca^{2+} contents in sodic water is shown in Fig. 2.

The relationship presented above is obviously inconsistent with the hydrolytic model of HCO_3–Na-water formation. At the same time, it suggests that a natural mechanism governing the Na^+ supply into solution and simultaneous Ca^{2+} removal exists in the Volga–Ural Basin.

The SO_4–Na-water ($M = 1.5$–20 g/dm^3) occurs at a depth down to 300–500 m in the difficult water circulation zone localized below the river drainage incision. Na^+ and Ca^{2+} dominate in the cation composition of water with $M < 6.5$ g/dm^3 (40–90% and up to 50%, respectively). Only Na^+(70–90%) is typical of water with $M > 6.5$ g/dm^3. The SO_4^{2-} content is 3.8–12.7 g/dm^3, i.e., 3–7 times higher than in typical gypsum (SO_4–Ca) water. The total amount of Na_2SO_4 reaches 10.3 g/dm^3. The reaction of medium is alkaline (pH = 7.4–8.8), Eh > 0, and $T = 5$–8°C.

Appearance of Na_2SO_4 in natural waters may be provided by different processes, including (1) extraction of sodium sulfate minerals (mirabilite, thenardite, and others), (2) mixing of SO_4–Ca- and HCO_3–Na-waters or reaction of the latter with $CaSO_4$, and (3) cation exchange between Na^+ of AC and Ca^{2+} of sulfate water (Posokhov, 1972). The Na_2SO_4 extraction is extremely problematic, because sodium sulfate is lacking in Upper Permian rocks. Reaction with the participation of $NaHCO_3$ and $CaSO_4$ under the existing conditions does not yield the SO_4–Na water with $M > 1.5$ g/dm^3.

The Cl–Na–Ca-brines ($M = 200$–330 g/dm^3) is the principal geochemical type of water in deep-seated subsalt complexes. They make up a spatially persistent hydrogeochemical zone reaching 5–7 km in thickness within basement depressions. The brines are characterized by a high metamorphism (rNa/rCl = 0.1–0.7; 20–80% $CaCl_2$), low sulfate content (rSO$_4 \cdot$ 100rCl = 0.02–0.70), enrichment in Br^- and REE, acid reaction of medium (pH = 5–7), negative Eh values ranging from –200 to –300 mV, and nitrogen–methane gas composition with a high He content (3–10 cm^3/dm^3). The Cl/Br ratio falls to 160–75 and rCa/rMg increases up to 20.

Researchers have proposed endogenic, infiltration, and sedimentogenic (thalassogenic) hypotheses for explanation of the genesis of Cl–Na–Ca-brines. They are reviewed in (Posokhov, 1977).

Lithological–hydrogeochemical investigations revealed that the exchange adsorption properties of terrigenous rocks and their role in the metamorphism of groundwater are differentiated with the depth of sedimentary basin. The most favorable environment for cation exchange is created at the upper stage composed of Upper Permian clayey rocks having a great AC capacity. The highest concentration of adsorbed cations (30–85 mmol/100 g) is detected in the finely dispersed clay and claystone. The exchange capacity of clayey sandstone and siltstone commonly is 20–40 mmol/100 g.

The high AC capacity is caused by the hydromica–smectite composition of the clay. Under hydrodynamically active conditions, the exchange adsorption bears a directed character and therefore exerts a strong metamorphic impact on groundwater composition. More than 2000 mmol (40 g) of cations may pass into 1 dm^3 of solution at the average AC capacity of 20–30 mmol/100 g and $n = 0.2$. This value is much higher than the actual concentration in the hydrated state (up to 250 mmol/dm^3 or 5 g/dm^3).

The composition of adsorbed bases is variable (25–95% Ca^{2+}, 3–47% Mg^{2+}, 1–60% Na^+, and 0.4–2.5% K^+). The depth-dependent relative amounts of alkali and alkali-earth elements are indicators of the genetic feature of AC.

The uppermost part of the section (0–50 m) corresponding to the zone of HCO_3–Ca-water is characterized by the predominance of Ca^{2+} (60–95% or 0.3–1.3 g/100 g) over Na^+ (1–7% or 0.01–0.1 g/100 g). The rCa/(rNa + rK) ratio is 11–46, which is typical of continental AC. Taking into account hydrochemical features of the Late Permian lithogenesis expressed in the abundance of saline and low-brine (sodic) water reservoirs, it can be concluded that the AC of rocks in this zone was regenerated from the marine-type AC with (rNa + rK) > rCa at the Mesozoic–Cenozoic subaerial stage of the basin evolution.

At a great depth within the zone of HCO_3–Na-water, the Na^+ concentration in AC increases to 0.4 g/100 g, whereas the Ca^{2+} concentration decreases to 0.3–0.1 g/100 g. The rCa/(rNa + rK) ratio is 0.9–1.3. The full consistence of cation compositions of AC and groundwater (Fig. 3) indicates that the water–rock cation exchange is the major process providing the formation of HCO_3–Na-water.

As was shown by physicochemical modeling (Popov *et al.*, 1992), HCO_3–Na waters of the Borzhomi and Yessentuki types with a higher mineralization ($M = 8$–15 g/dm^3) may be formed by ion exchange in terrigenous (clayey) carbonatized rocks with the Na-type AC as a result of reaction with carbonated water ($CO_2 = 1$–3 g/cm^3) in the absence of a great amount of sulfates and chlorides as solid phases. These conditions are inherent in young (Kimmerian–Alpine) orogens and plates (Caucasus, Ciscaucasus region, western Siberia, and others), where carbon dioxide is generated in the course of thermal metamorphism and magmatic activity and then incorporated into marine sedimentary rocks by ascending migration.

The gypsum-bearing terrigenous rocks in the zone of SO_4–Na-water ($M \leq 20$ g/dm^3) contain still higher concentrations of adsorbed Na^+ (0.22–0.56 g/100 g) (Fig. 3). The rCa/(rNa + rK) ratio is commonly 0.83–0.97. At the same time, typical SO_4-Ca-solutions with $M = 2$–3 g/dm^3 are formed in the terrigenous gypsum-bearing sequences depleted in adsorbed Na^+. These data unequivocally testify to the exchange adsorption nature of the SO_4–Na-water. Therefore, we believe that

the main point in the issue of the genesis of SO_4–Na-waters with $M = 5$–20 g/dm^3 consists in elucidation of a mechanism that provides the Na_2SO_4 gain in solution rather than estimation of the role of cation exchange in their formation (this is obvious). In other words, the issue is as follows: how the SO_4–Na-water with a much higher mineralization is formed from the SO_4–Ca-water with $M = 2$–3 g/dm^3 during the stoichiometric exchange adsorption reaction? According to the commonly accepted point of view (M.A. Al'tovskii, S.A. Durov, E.V. Posokhov, and others), the mineralization formed as a result of cation exchange in water should not substantially be distinct from the mineralization of the primary solution subjected to metamorphism.

Methods and results of the experimental works focused on the genesis of SO_4–Na-waters have been described in detail in the previous work (Popov *et al.*, 1992). It should only be stated here that like in the case of highly mineralized sodic carbonated water, the gypsum extraction and ion exchange of Ca^{2+} of water by adsorbed Na^+ are not one-stage processes in the hydrodynamically mobile environment. They bear a multistep progressive character providing the gain of a great amount of Na_2SO_4 in solution. Owing to these interrelated and complementary processes stimulating each other (cation exchange that promotes the generation of Na_2SO_4 in solution and extraction of a new portion of $CaSO_4$ by the newly formed SO_4–Na-water), the highly mineralized sodium sulfate water is produced. Therefore, the notion on equal mineralization of the initial and final solutions during ion exchange is only valid for static conditions when this process is realized in a single water body.

However, even in this situation, despite large resources of gypsum and adsorbed Na^+ in rocks, increase in the M value of solution and accumulation of Na_2SO_4 therein occurs only to certain limits. In experiments, these limits are 10–12 and 9.0–9.5 g/dm^3, respectively. This is related to decrease in the solubility of $CaSO_4$ (from 1.46 to 0.44 g/dm^3 in experiments) and the amount Na^+ removed from AC into solution (from 92 to 12 $mg/100$ g) and the consequent attenuation of ion exchange. At $M = 15$–17 g/dm^3 (close to the M limit for the SO_4–Na-water in the region), the $CaSO_4$ dissolution ceases and the lithological–hydrogeochemical system Na_2SO_4 (solution)–$CaSO_4$ (rock)–AC attains equilibrium.

At deep levels of basins (>1000–1500 m), which correspond to zones of very difficult water exchange and quasistagnant regime (with respect to hydrodynamics) or the lower zone of supergenesis and zones of catagenesis and metagenesis (with respect to lithology and geochemistry), the influence of ion exchange on the brine composition is inevitably weaker, because the AC capacity of Paleozoic and Upper Proterozoic rocks abruptly decreases to 5–1 $mmol/100$ g along with increase in their mineralization up to 300–350 g/dm^3.
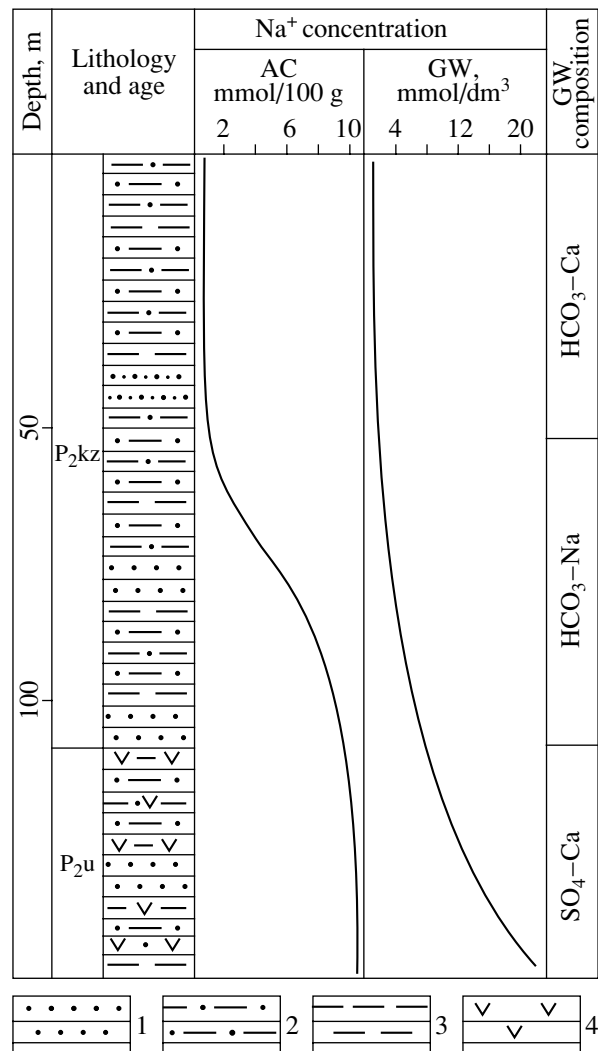

Fig. 3. Variation of Na^+ concentration in AC and groundwater (GW) of Upper Permian rocks with depth. (1) Sandstone, (2) siltstone, (3) claystone and clay, (4) gypsum.

This is caused by the lithification of rocks, simplification of clay mineral structure in the smectite–hydromica–chlorite series, and physicochemical conditions of deeply subsided basinal zones. These processes are governed by *PT* parameters and geologic time that are responsible for the aging of colloids and their transition into unchangeable state.

Figure 4 shows the typical lithological–hydrogeochemical situation of the Volga–Ural Basin, i.e., cation concentration in the groundwater increases with depth from fractions to 5 mol/dm^3. The porosity and AC capacity decrease from 0.3 and 30 $mmol/100$ g, respectively, at the surface to 0.1 and 1 $mmol/g$ at a depth of 5 km. The intersection of curves describing the behavior of hydrated and adsorbed cations is localized at a depth of ~800 m. Taking into account a certain variation of n and AC capacity, the intersection point is not rigidly fixed and may vary within a range of 700–1000 m.
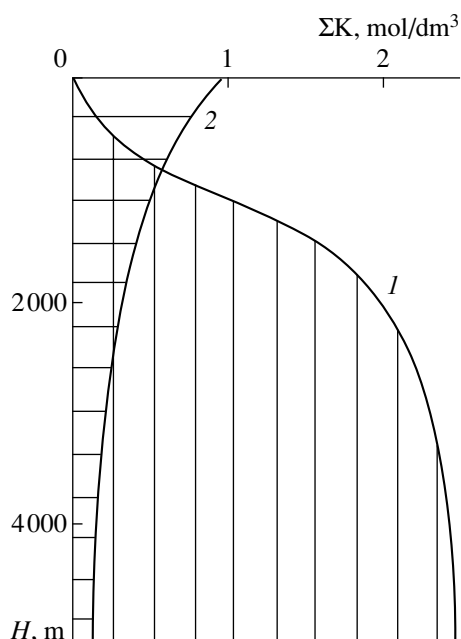
Fig. 4. Variation of hydrated cation concentration (curve *1*) and concentration of adsorbed cations removed from AC into groundwater (curve *2*) with depth.
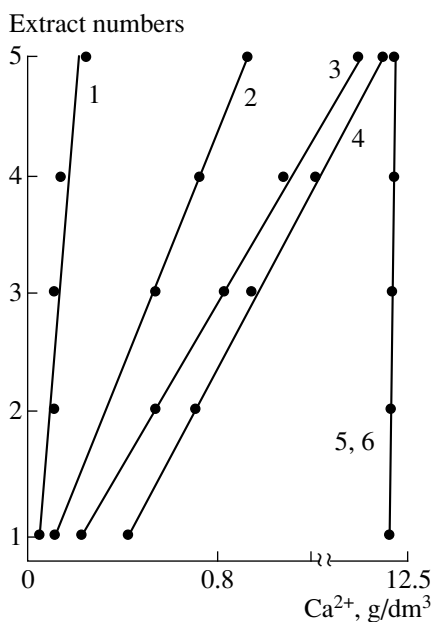
Fig. 5. Behavior of Ca^{2+} in model solutions. Runs modeling the interaction of: (1) Cl–Na-brine with Middle Carboniferous claystone, (2) Cl–Na-brine with Lower Carboniferous claystone, (3) Cl–Na-brine with Middle Devonian claystone, (4) Cl–Mg-brine with Middle Carboniferous claystone, (5, 6) Cl–Ca–Na-brine with Lower and Middle Carboniferous claystones.

The AC capacity of overlying rocks is quite sufficient for the complete metamorphism of water with $M < 50$ g/dm^3. At a great depth, the mass of adsorbed

cations, which may potentially be removed from the AC into groundwater, cannot provide the formation of cation composition not only in brines, but also in saline water.

The calculation results agree well with experimental results on the metamorphism of Cl–Na–Mg- ($M = 100$ g/dm^3), Cl–Na- ($M = 200$ g/dm^3), and Cl–Ca–Na- ($M = 240$ g/dm^3) brines in Middle Devonian and Lower–Middle Carboniferous terrigenous rocks. The AC value is 4–12 mmol/100 g. The adsorbed ions mainly consist of Ca, as suggested by rCa/(rNa + rK) = 4–10. The fivefold brine extracts from fresh charges of rocks, which were crushed and washed to remove readily soluble salts, were prepared and analyzed (the liquid/solid phase ratio in the charges was 2 : 1).

The experimental results confirmed that the interaction between the above phases does not give rise to an appreciable Ca^{2+} gain (Fig. 5). The Ca^{2+} concentration in Ca-depleted Mg- and Na–Mg-brines of final extracts was only 0.3–1.8 g/dm^3 (0.4–6.4%). In experiments with the most concentrated Ca–Na brine, the Ca^{2+} content did not increase at all and remained at the initial level (12.2 g/dm^3). The AC composition in rocks participating in reactions also did not change.

LITHOLOGICAL–HYDROGEOCHEMICAL IMPLICATIONS OF METASOMATIC DOLOMITIZATION

The exchange adsorption in carbonate and terrigenous rocks largely proceeds at the lower stage of sedimentary basins. As was mentioned above, the abundance of terrigenous sediments in the sub-Kungurian Paleozoic of the study region is minor, relative to carbonate rocks. Therefore, like reactions of exchange adsorption in aluminosilicates, albitization and analcimization cannot appreciably alter the composition of deep-seated brines.

Under lithological–mineralogical conditions of the Volga–Ural Basin, the formation of Cl–Na–Ca-brines is mainly governed by the metasomatic dolomitization of Paleozoic and Upper Proterozoic limestones rather than the adsorption and absorption. The dolomitization is driven by the density convection of heavy ($\rho = 1.29$–1.37 g/cm^3) mother Cl–Mg-brines, which are mainly delivered from Permian evaporite reservoirs, into lighter ($\rho = 1.02$–1.13 g/cm^3) thalassogenic Cl–Na-brines. The process takes place according to the principle of convection cell and is accompanied by a partial mixing of waters with different compositions and expulsion of formation fluids into the sedimentary basin (Popov, 2000).

The ability of solutions to dolomitize limestones is assessed by an equation derived from the law of mass action: $\alpha_{Mg}^{2+}/\alpha_{Ca}^{2+} = rMg/rCa \cdot \gamma_{Mg}^{2+}/\gamma_{Ca}^{2+} = SPd/SPc$, where α_{Ca}^{2+} and α_{Mg}^{2+} are activities of Ca^{2+} and Mg^{2+} ions, rCa and rMg are concentrations of Ca^{2+} and Mg^{2+}

ions (mol/dm³), γ_{Ca}^{2+} and γ_{Mg}^{2+} are activity coefficients of Ca^{2+} and Mg^{2+} ions, SPc and SPd are solubility products of calcite and dolomite, respectively.

If the ratio of Mg^{2+} and Ca^{2+} ($\xi = \alpha_{Mg}^{2+}/\alpha_{Ca}^{2+}$) activities ($\xi = \alpha_{Mg}^{2+}/\alpha_{Ca}^{2+}$) is more than the ratio of solubility products of dolomite and calcite ($\xi >$ SPd/SPc), the formation of dolomite owing to the replacement of Ca^{2+} in the crystalline lattice of calcite by Mg^{2+} of brine is the most probable process. In the opposite case, the solution is undersaturated with $CaCO_3 \cdot MgCO_3$, and dissolution of solid phase (dolomite) or decrease in dolomitization rate is possible in carbonate rocks.

The thermodynamic analysis of the capacity of various geochemical types of brines in the study region to dolomitize limestones gave the following results. The highest ξ value (>100–400) is typical of the Cl–Mg-brine at the gypsum and halite precipitation stage (in the normal seawater, $\xi = 5.6$). The ξ value has a direct correlation with Mg^{2+} concentration in solution and rMg/rCa. The SPd/SPc ratio in brines of this type is 13.4–13.7, and ξ is more than one order of magnitude higher than SPd/SPc. Hence, the Cl–Mg-brines have a high capacity to form metasomatic dolomites.

The sedimentary and epigenetic subsalt Cl–Na–Ca-brines have a very low rMg/rCa value (0.05–0.20). The ξ value of alkali-earth components in these brines is 0.16–0.33, i.e., one to two orders of magnitude lower than SPd/SPc. This indicates that dedolomitization, i.e., decrease of Mg^{2+} in dolomitized limestone and dolomite, is theoretically possible. However, this process was apparently insignificant in the hydrodynamically passive environment, and the carbonate rock–Cl–Na–Ca-brine system is close to thermodynamic equilibrium at the present geologic epoch.

Infiltrational Cl–Na-brines of leaching with low ξ values (0.56–0.83) also cannot form the metasomatic dolomite.

Long-term metasomatic processes gave rise to the drastic alteration of subsalt carbonate sequences in the Volga–Ural Basin. We carried out the quantitative lithological–hydrogeochemical estimation of dolomitization for the southeastern part of the Volga–Ural Basin with an area of 100000 km². The secondary (dia- and epigenetic) dolomites occur throughout the entire Paleozoic–Upper Proterozoic section in this territory. They are most widespread in the Lower Riphean, Upper Devonian–Tournaisian, Visean, Moskovian, and Sakmarian (Lower Permian) rocks. They bear obvious signs of secondary alteration (metasomatic replacement of calcite by dolomite, highly variable extent of dolomitization, and its selective character depending on structural and genetic features of limestones).

The thickness of dolomitized rocks ($h$dr) in particular Paleozoic stratigraphic units varies from a few meters to 140 m and reaches several hundreds of meters in the Riphean. Their total thickness (Σhdr) in the Pale-

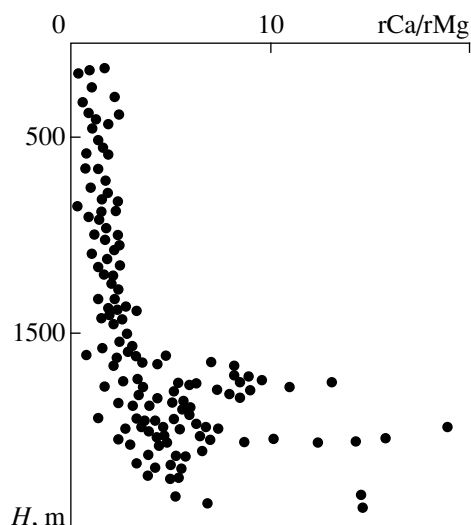**Fig. 6.** Variation of rCa/rMg ratio in brines with depth.

ozoic varies from 160 to 400 m, i.e., occupies 5–27% of the entire Paleozoic section. Ronov (1956) estimated the Mg^{2+} content in rocks as 1–10% (5%, on the average). This value equals 13.2% for the pure chemogenic dolomite.

The mass of dolomitized rock block ($m$dr) with Σhdr = 300 m, area s = 100000 km², and rock density $\rho = 2.8$ t/m³ is 300 m × 10^{11} m² × 2.8 t/m³ = 8.4 × 10^{13} t while the amount of Mg^{2+} therein is mMg = 8.4 × 10^{13} t × 0.05 = 4.2 × 10^{12} t.

Since the metasomatic replacement of calcite by dolomite proceeds in equivalent quantities and the Ca^{2+} atomic mass is higher than that of Mg^{2+}, the amount of Ca^{2+} passing into liquid phase will be slightly greater than the above estimate. Let us compare it with the actual Ca^{2+} mass in Paleozoic and Proterozoic Cl–Na–Ca-brines.

In the Paleozoic sequence, the average thickness of the zone with Cl–Na–Ca-brines hPZ = 2000 m. The average Ca^{2+} concentration C_{Ca}PZ = 25 g/dm³. The respective parameters of the Proterozoic sequence are 4000 m and 40 g/dm³.

The volume of Cl–Na–Ca-brines in Paleozoic rocks with porosity n = 0.05, hPt = 2000 m and s = 100000 km² is estimated as VPZ = 2 km × 100000 km² × 0.05 = 10^4 km³; the Ca mass therein is m_{Ca}PZ = 10^{13} m³ × 25 kg/m³ = 2.5 × 10^{11} t. In Proterozoic rocks, VPR = 4 km × 100000 km × 0.05 = 2 × 10^4 km³; m_{Ca}PR = 2 × 10^{13} m³ × 40 kg/m³ = 8 × 10^{11} t. The total amount of Ca^{2+} in brines of the sedimentary sequence is $\Sigma m_{Ca} \sim 10^{12}$ t.

Thus, the amount of Ca^{2+} released from limestones as a result of dolomitization is quite enough to form Cl–Na–Ca-brines in the sedimentary cover.

It is noteworthy that the most metamorphosed Cl–Na–Ca-brines in the present-day Volga–Ural Basin

have a very high rCa/rMg value (4–20), indicating that the replacement of Ca in limestone by Mg of brines has been completed long ago (Fig. 6).

CONCLUSIONS

The results obtained show that ion exchange interactions in the heterogeneous water–rock system bear a distinct zonal character and exert a great influence on the lithological–hydrogeochemical state of sedimentary basin. Processes of exchange adsorption in Upper Permian terrigenous sediments with a marine signature of adsorbed complex played the crucial role in the formation of HCO_3–Na- and SO_4–Na-waters in the supergene zone (down to a depth of 300–500 m).

The formation of Cl–Na–Ca-brines, which prevail in catagenetic and metagenetic zones (depth >1000–1500 m), was caused by concentration convection of the mother Cl–Na–Mg-brine largely delivered from Early Permian evaporite basins to underlying Paleozoic and Upper Proterozoic rocks. The convective subsidence of highly mineralized saliferous brines into the terrigenous and carbonate environment was accompanied by exchange adsorption. Metasomatic dolomitization of limestones played the principal role in the metamorphism of brines. These processes apparently started in the Devonian when the first evaporite basins appeared. However, they were most intensive during the existence of the Permian saliferous basin ranging from $n \times 10^4$ to $n \times 10^5$ yr. After that, the epigenetic alteration of saliferous, carbonate, and terrigenous rocks lasted for a long geologic time.

ACKNOWLEDGMENTS

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