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Water–Rock Interaction in Vendian Sandy–Clayey Rocks of the Mezen Syneclise

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Abstract—Based on specific features of the geological structure and hydrogeological conditions of the Mezen Syneclise, the trend and quantitative estimates of compositional changes of groundwaters in Vendian sandy–clayey rocks in different hydrodynamic zones are given.

The composition of groundwater and hosting sandy–clayey rocks at initial stages of their existence are defined by the nature of provenances and hydrochemical characteristics of the environment of sedimentary basins. The subsequent interaction of rocks with groundwaters leads to changes in both mediums. Main regularities of this process are studied in (Zverev, 1982; Shvartsev, 1991; and others). However, final results of the water–rock interaction significantly differ in various regions characterized by specific features of geological development. Interpretations of their evolution are sufficiently complex and ambiguous. At the same time, their reconstruction is an essential task, because it allows us to reveal the role of various geological factors, including those that are responsible for the formation of commercial mineral deposits.

This work presents an attempt to analyze changes of the chemical composition of groundwaters in Vendian sandy–clayey rocks of the Mezen Syneclise on the basis of paleohydrogeological reconstructions.

SPECIFIC FEATURES OF THE GEOLOGICAL STRUCTURE OF THE MEZEN SYNECLISE

The Mezen Syneclise is a vast depression located in the northern Russian Plate. It is bounded by the Baltic Shield in the west and the Kanin–Timan Foldbelt in the east. The syneclise merges with the Moscow Syneclise via the Middle Russian aulacogen in the south (Fig. 1).

The crystalline basement has Archean–Early Proterozoic age within a larger part of the syneclise. The basement consists of intensely dislocated and strongly metamorphosed gneisses, granite gneisses, amphibolites, and crystalline schists. Shales of Baikalian (Riphean) complex are found only in the northeastern area of the syneclise (Pesha Basin).

The formation of the Mezen Syneclise is closely related to processes of the Riphean rifting at the northeastern margin of the Russian Plate and its subsidence in the Late Vendian above the system of Riphean paleorifts. Therefore, the basement is broken into blocks expressed in the topography as Riphean depressions and horsts. These structures mostly extend in the northwestern direction and make up a branched network of rift grabens.

The sedimentary cover of the Mezen Syneclise includes Middle–Upper Riphean, Upper Vendian, Paleozoic, Mesozoic, and Cenozoic rocks (Fig. 2).

Riphean rocks make up the base of the sedimentary cover and are developed over the entire territory of the syneclise, but their most complete sections are observed in the rift depressions. On basement highs, the Riphean rock sequence is sharply reduced up to the point of their complete pinchout. Their occurrence depth varies from tens of meters near the White Sea coast to 2–2.5 km in the eastern part of the syneclise. The maximal recovered thickness is 1964 m (Ust-Mezen Rift).

On the whole, the complete Riphean sequence, about 2 km thick, includes two (Middle and Upper Riphean) cycles. The lower cycle is mainly composed of mudstones with interlayers of marls, dolomites, and sandstones. The upper cycle is dominated by sand. The mudstones contain fine-dispersed organic matter. Riphean rocks in deep zones are pyritized, whereas sandstones lying at a depth of about 300 m close to the Baltic Shield contain abundant iron hydroxides. The Riphean sequence includes volcanic rocks (basalts and dolerite basalts) and volcaniclastic breccia.

Vendian rocks with angular unconformity overlie the Riphean sequence. These rocks are universally spread in the Mezen Syneclise and represented by the upper series including the Ust-Pinega (Redkino Horizon), Mezen, and Padun (Kotlin Horizon) formations. Their total thickness (674–1388 m) has been recovered in the eastern part of the syneclise at a depth of 700–1500 m. The base of the Vendian sequence lies at a depth of 1840–2530 m. In the Pesha Depression, the

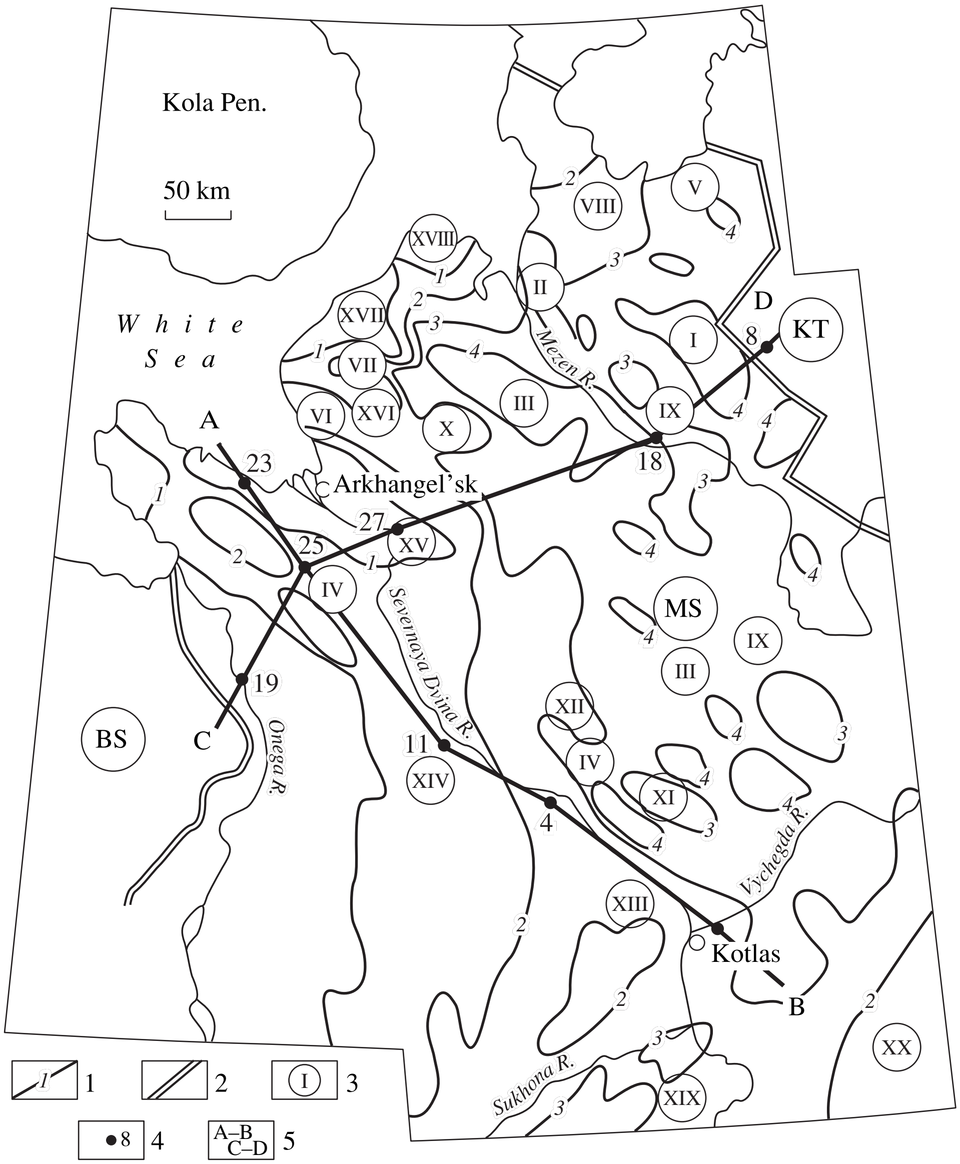

Fig. 1. Structural scheme of basement of the Mezen Syneclise. Modified after (*Tectonicheskaya…,* 1998). (1) Isobase lines of the Mezen Syneclise basement, km; (2) boundaries between the Baltic Shield, Mezen Syneclise, and Kanin–Timan Foldbelt; (3) basement structures: (BS) Baltic Shield, (MS) Mezen Syneclise, (KT) Kanin–Timan Foldbelt; rifts and depressions: (I) Safonov, (II) Ust-Mezen, (III) Leshukon–Pinega, (IV) Onega–Toem, (V) Pesha, (VI) Kerets, (VII) Padun; uplifts and ridges: (VIII) Nes–Tylug; (IX) Mezen–Vashkin; (X) Poltin–Ezhug; (XI) Uftyug, (XII) Yul; (XIII) Krasnobor, (XIV) Vazha, (XV) Arkhangel'sk, (XVI) Zolotitsa, (XVII) Ruch'ev, (XVIII) Kuloi; (XIX) Middle Russian Aulacogen; (XX) Sysol Dome; (4) borehole and its number; (5) hydrochemical profiles.

Vendian sequence is encountered at a depth of 1790–3252 m. Therefore, its base may be located at a depth of 3–4.5 km. In the western part of the syneclise, the Vendian rocks are observed at depths ranging from 0 to 50–300 m. Their thickness reduces from 1213 to 0 m.

The composition of Vendian rocks has been scrutinized in the western part of the Mezen Syneclise. The Ust-Pinega Formation (up) of this area is divided into the Tamitsa, Lyamitsa, Arkhangel'sk, Verkhov, Syuz'ma, Vaizitsa, and Zimnegorsk beds (Stankovskii *et al.*, 1981).

The Tamitsa Bed (tm) includes varigrained poorly sorted sandstones composed of K-feldspar (partly kaolinitized), quartz, and subordinate mica. The gritstone content in the sequence can attain 30%. Kaolinite predominates in the composition of clay minerals. The cement is ferruginous–clayey, more rarely carbonate. The weakly cemented sandstones contain sand at some intervals (up to 40% of the total thickness). Thickness of the Tamitsa Bed is 30 m.

The Lyamitsa Bed (lm) chiefly consists of hydromicaceous mudstones with an insignificant admixture of

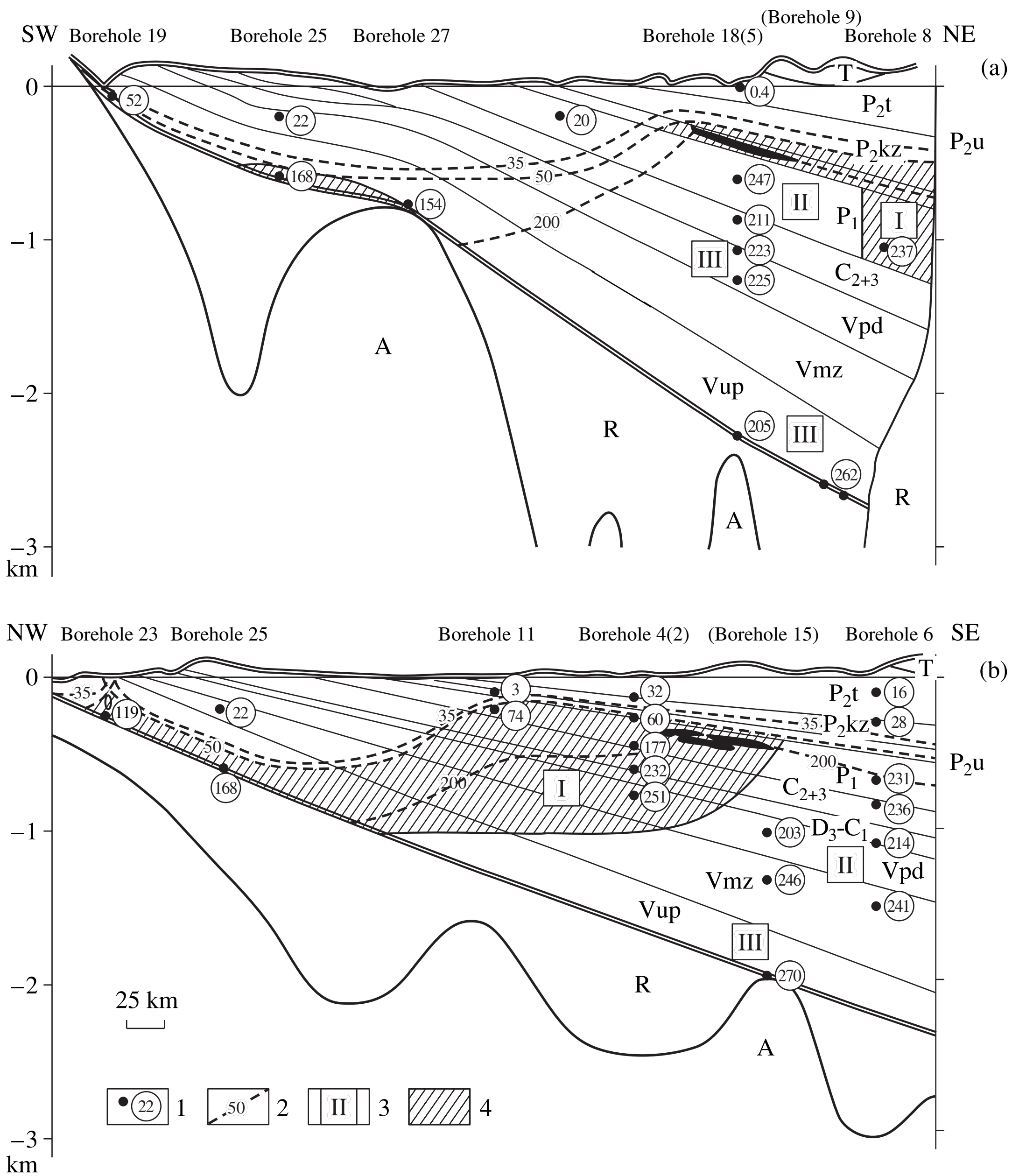

Fig. 2. Hydrochemical profiles: (a) across the strike of the major paleorifts; (b) along the Onega–Toem rift zone. (1) TDS content in water at sampling site (g/l); (2) isolines of water salinity; (3) brine type: (I) high-Na, (II) low-Ca, (III) high-Ca; (4) domain of type I brines.

smectite and kaolinite. Cracks, up to 1 mm wide, are locally filled with calcite. The presence of thin (1–3 mm, more rarely up to 5 cm) interlayers of ash tuff (Na-smectite) is a characteristic feature. The mudstones also contain an admixture of tuffogenic material. Thickness of the Lyamitsa Bed is 30 m.

The Arkhangel'sk Bed (ar) is composed of mudstones with rare interlayers of siltstones and sandstones that account for 1–10% of the total thickness. The sand content is maximal in the upper (~50-m-thick) part of the sequence, where the sandstones account for up to 25% of the section. The mudstones mainly consist of pelitic particles of hydromica, (60–90%), with a local smectite admixture. The silt fraction is composed of quartz, feldspars, and the subordinate micas, chlorite, calcite, and dolomite. The fine-grained siltstones are composed of feldspar and quartz. The clastic material (60–80%) consists of quartz, feldspars, micas, and chlorite. The cement has carbonate–clayey and clayey-carbonate compositions. The clayey component is represented by hydromica and mixed-layer hydromica–smectite minerals. The content of heavy fraction is less than 1%. Authigenic pyrite and micas are widespread. The Arkhangel'sk sequence is characterized by the predominance of Fe^{2+} over Fe^{3+} and high contents of bitumen and C_{org}. Thickness of the Arkhangel'sk Bed is 150 m.

The Verkhov Bed (vr) includes mudstones with tuff interlayers. Relative to the Arkhangel'sk Bed, the Verkhov Bed is marked by some prevalence of Fe^{3+} over Fe^{2+} and drastic decrease of bitumen and C_{org} contents. The pelitic fraction is mainly composed of hydromica with some smectite admixture. Thickness of the Verkhov Bed is 30 m.

The Syuz'ma Bed (sz) consists of mudstones and siltstones. Relative to the Arkhangel'sk Bed, Syuz'ma Bed has a more variable composition of pelitic particles and cement. The hydromicas are supplemented with abundant carbonate–chlorite–clay, clay–carbonate, and smectite materials. In the heavy fraction, the pyrite content is 2.4 times lower, while the content of black ore minerals, mica, and chlorite is 2–3 times higher. The average content of bitumen and C_{org} is diminished. Thickness of the Syuz'ma Bed is 50 m.

The Vaizitsa Bed (vz) is composed of mudstones analogous to those of the Lyamitsa and Verkhov beds. However, it is characterized by higher pyrite content (up to 60%) in the heavy fraction of silty varieties. Thickness of the Vaizitsa Bed is 30 m.

The Zimnegorsk Bed (zm) includes green-colored rocks (siltstones and the major mudstones). The upper part of this sequence (~100 m thick) contains interlayers of fine-grained sandstones (0.2–0.7 m) that account for 20–30% of the sequence. The pelitic component of the mudstones is composed of the major hydromicas and the subordinate smectite, carbonate–chlorite–clay material, and kaolinite. The majority of silt-sized particles are composed of quartz, feldspars, and micas. The carbonate-clayey (hydromicaceous) cement accounts for up to 25–40% of the siltstones. The content of clastic particles (quartz, feldspars, and micas) in the sandstones is 55–60%. The cement is composed of carbonate and clay–carbonate materials. The content of heavy fraction is 1.7%. Pyrite accounts for up to 25% of the heavy fraction. Thickness of the Zimnegorsk Bed is 160 m.

The Mezen Formation (mz) includes the Ergin and Mel'sk beds. The Ergin Bed (er), 100 m thick, includes intercalation of mudstones (35–40%), siltstones (35–40%), and sandstones (20–30%). The lower part of the sequence has a gray-green color. Reddish brown interlayers appear in the upper part of the sequence and account for up to 50%. The Mel'sk Bed (ml), 150 m thick, is characterized by the alternation of lithologically similar but varicolored-rocks (completely red in some sections). In the pelitic fraction of mudstones of the Mezen Formation, hydromicas are supplemented with a significant amount of kaolinite (Mel'sk Bed), chlorite, and iron hydroxides. The content of iron hydroxides increases and smectites disappear upward the section. The silty fraction includes quartz, feldspars, and the subordinate micas. Mudstones of the Mezen Formation are composed of feldspars and quartz. The cement has a mixed composition (hydromicas, chlorite, carbonate, kaolinite, and iron hydroxides). The sandstones have a fine-grained structure with a variable content of clay. The clastic particles consist of quartz (80–90%), feldspar (5–20%), and mica (1–3%). The cement is composed of carbonate–chlorite–clay and clay–carbonate–gypsum materials. Clay minerals are represented by hydromicas and kaolinite. Iron hydroxides are abundant. Relative to the Zimnegorsk Bed, the Mezen Formation is depleted in the heavy fraction. The authigenic pyrite, which dominated in the Ust-Penega Formation, is almost absent here.

The Padun Formation (pd), 160 m thick, mainly consists of sandstones (60–80%) and siltstones (20–30%) separated by mudstone interlayers. The rocks have reddish brown color with pale green lenses and patches. The sandstones are dominated by fine- and medium-grained varieties. The content of pelitic particles does not exceed 20%. Clastic material is represented by quartz. Feldspars, chalcedony, quartzite fragments, biotite, and clayey aggregates are insignificant. The cement has mainly clayey (hydromicaceous)–ferruginous composition. Carbonate and gypsum cement is also encountered. In the upper part of the sequence (thickness ~50 m), the sandstones are poorly cemented and often represented by sands. The siltstones are dominated by the coarse-grained fraction. The clastic grains consist of quartz (up to 98%), feldspars (up to 10%), and micas (~1%). The cement has clayey–ferruginous, carbonate–clayey, and less common gypsum compositions. Clay minerals are observed as hydromicas, kaolinite (increasing upward the section), and chlorite (decreasing upward the section up to the point of disappearance). Siltstones are mainly composed of hydromicas, iron hydroxides, and chlorite. The content of quartz and feldspar particles is 10–15%. The content of carbonates in rocks of the Padun Formation is minimal for the entire Vendian sequence, except for the Tamitsa Bed. Proportion of ferrous and ferric iron is almost the same as in the Mel'sk Bed. Bitumen and organic carbon are nearly absent.

The **Paleozoic sequence** is composed of Silurian, Devonian, Carboniferous, and Permian rocks.

Silurian rocks are confined to the Pesha Depression.

Devonian rocks are mainly found on the left bank of the Severnaya Dvina River and Timan region. In the Severnaya Dvina area, Devonian rocks, 13–32 m thick, are located at a depth of 146–1065 m. They consist of fine- to medium-grained sands and loose sandstones with clay interlayers. The clay has hydromicaceous and calcareous compositions. Salt domes have been recovered at a depth of 231–580 m in the northern area of Syktyvkar. The Upper Devonian Seregovo saliferous sequence, which extends to a depth of 1125 m in the stock within the salt domes, consists of dolomite, clay, and halite.

Lower Carboniferous rocks (clays and siltstones with thin interlayers of carbonate rocks) are found only on the left bank of the Severnaya Dvina River. The Middle Carboniferous (Moscovian) sequence is composed of terrigenous–carbonate rocks of the Kashira Horizon and carbonate rocks of the Podol'sk and Myachkovo horizons. The Upper Carboniferous sequence (up to 10–98 m thick) includes carbonate rocks with gypsum and anhydrite interlayers (Kasimovian and Gzhelian stages).

The Lower Permian sequence consists of carbonate rocks with gypsum and anhydrite interlayers (~80 m). These rocks also fill the Dvina–Sukhona saliferous basin (*Istoriya…*, 1981) situated in the interfluve of these rivers (Fig. 1). Rock salt occurs at depths ranging from 250 to 700 m (Fig. 2). Upper Permian rocks include celestine.

Mesozoic rocks are locally developed in the eastern part of the Mezen Syneclise.

The **Cenozoic sedimentary cover** is characterized by the predominance of Quaternary glacial deposits. The Quaternary cover is generally thin. However, the thickness increases to 20–100 m on coastal lowlands (due to the presence of clays of the Mikulino Interglaciation) and reaches 100–250 m in paleovalleys. River valleys, which cut the Quaternary cover to a depth of 50 m, are filled with sandy–clayey sediments.

HYDROGEOLOGICAL STRUCTURE OF THE MEZEN SYNECLISE

The vertical (hydrodynamic and hydrochemical) zonality of groundwaters is defined at first approximation by filtration properties of water-enclosing rocks, the depth of their occurrence (intensity of draining influence on surface streams and basins), and the openness of recharge and discharge areas (presence of regional aquicludes). The influence of all of these factors must be considered for the entire geological history of the region.

Changes in filtration properties of rocks across the sedimentary cover are shown in Tables 1 and 2. High filtration properties (k_f = 0.6–1.0 m/day) are typical of near-surface sediments lying at an absolute mark of more than –100 m. This is the **active water-exchange zone** (hereafter, AWE zone). The filtration rate in this zone is not lower than 10^{-1}–10^{-2} m/day at a hydraulic gradient of 0.01–0.001. The time of complete water exchange at such filtration rates and active porosity $n_0 = 0.25$ is not more than 10^2–10^3 yr if the distance between the recharge and discharge zones is approximately 10 km. For the Vendian rocks located in the western part of the Mezen Syneclise (interval from –100 to –600 m), k_f = 0.03–0.01 m/day. Here, the filtration rate decreases to 10^{-3}–10^{-4} m/day, and the time of complete water exchange increases up to 10^4–10^5 yr if the filtration distance is approximately 100 km. Thus, the Vendian sequence approximately corresponds to the

Table 1. Filtration properties of post-Riphean rocks (interval 0–1000 m)

Stratigraphic subdivision	Thickness, m	Filtration coefficient, m/day	Water conductivity, m²/day
N-Q	100	10^{-4}	0.01
	250	1	250
	50	5	250
J	50	2×10^{-4}	0.01
T	100	0.5	50
P_2t	200	0.5	100
P_2kz	150	7	1050
P_2u	50	1	50
P_1ar-kg	70	10^{-4}	0.01
$C_{2+3} - P_1a$-s	50	50	2500
	150	7	1050
C_2ur	30	3.5	105
iD_3-C_2	40	1	40
	550	0.01	5.5
	550	10^{-4}	0.06
Vpd	200	1	200
Vmz	250	0.03	7.5
Vu-p (zm)	100	0.01	1
Vu-p (lm-sz)	400	10^{-4}	0.04
Vu-p (tm)	25	1	25

relatively active water-exchange zone (hereafter, RAWE zone). In the eastern part of the Mezen Syneclise, the RAWE zone is composed of Upper Permian–Mesozoic rocks and restricted in depth by the regional aquiclude of Lower Permian gypsum and anhydrite (hereafter, Lower Permian aquiclude) with $k_f = 10^{-4}$ m/day (Table 1, Fig. 2) rocks.

The presence of fresh infiltration water is typical of the AWE zone. Areas with outcrops of Permian gypsum-bearing rocks are characterized by the presence of brackish waters.

The RAWE zone is marked by the presence of brackish and salt waters with TDS content less than 35 g/dm³ (Fig. 2); i.e, this zone is characterized by the penetration of fresh infiltration waters and the dilution of marine (sedimentogenic) waters and brines. This zone also includes the domain of type I brines (Table 3, Fig. 2) that can be traced down to a depth of approximately 1 km. These brines are related to the dissolution of Permian rock salts by infiltration waters (Malov, 2001b). They are found in areas where the Lower Permian aquiclude is eroded or perforated.

The remaining part of the sedimentary cover of the Mezen Syneclise is occupied by brines of types II and III (Table 3, Fig. 2). The Permian age of type II brines has been determined by the paleohydrogeological,

Table 2. Changes in filtration properties of Vendian and Riphean rocks with depth

Padun Fm., Vendian				Mezen Fm., Vendian			
Interval, m	k_f, m/day	km, m^2/day	n_0, %	Interval, m	k_f, m/day	km, m^2/day	n_0, %
0–200	1	200	25	200–450	0.03	7.5	15
782–879	0.1	25	20	983–1922	0.004	2	10
1443–1805	0.05	20	14	1805–2445	0.001	0.6	9
Ust-Pinega Fm., Vendian				Riphean			
Interval, m	k_f, m/day	km, m^2/day	n_0, %	Interval, m	k_f, m/day	km, m^2/day	n_0, %
450–950	0.002	1.04	10	1944–2814	0.001	0.3	6.5
1420–2220	3×10^{-4}	0.11	7	2252–3341	2×10^{-4}	0.14	1.2
2445–2833	6×10^{-5}	0.02	4	2646–2682	10^{-5}	0.006	3.6

Note: (k_f) Filtration coefficient of filtration; (km) water conductivity; (n_0) active porosity.

Table 3. Average composition of the major types of brines in the Mezen Syneclise (mg-eq.%) and their genetic coefficients (average values)

Brine type	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	rNa/rCl	Br/0.001Cl	Ca/Cl
I	87	9	4	96	4	0.9 (0.81–1.07)	1 (0.08–1.53)	0.06 (0.008–0.1)
II	75	17	8	99	1	0.73 (0.65–0.85)	4 (2.97–4.96)	0.11 (0.05–0.14)
III	55	36	9	99	1	0.52 (0.47–0.65)	5.7 (2.9–8.81)	0.19 (0.15–0.28)

Note: Range of values is given in parentheses.

kinetic-geochemical, and helium-argon methods (Korotkov, 1983; Popov, 1994). These brines were preserved owing to the screening role of the Lower Permian aquiclude. Hence, their domain is characterized by a longer time of complete water exchange (more than 250 Ma) at filtration rates ~10^{-5}–10^{-6} m/day. This is identified as the **difficult water exchange zone** (hereafter, DWE zone). Vendian rocks in this zone lie at depths more than 1 km and have significantly lower filtration and capacity properties (Table 2).

Type III brines, especially those in sandstones of the Vendian Tamitsa Bed and the Upper Riphean Uftyug Formation, which are screened from above by the regional aquiclude of mudstones of the Vendian Ust-Pinega Formation (hereafter, Vendian aquiclude), differ from type II by a significantly higher metamorphism grade (Malov, 2001b), suggesting their older (Late Devonian) age. The time of their complete water exchange is more than 360 Ma. This is possible at filtration rates ranging from 10^{-7} to -10^{-8} m/day and the predominance of diffusion mass exchange (Zverev, 1982). This is identified as the **very difficult water exchange zone** (hereafter, VDWE zone). Convective mass transfer prevails in all of the remaining hydrodynamic zones.

The formation of hydrogeological zonality in the Mezen Syneclise is related to its geodynamic evolution characterized by the predominance of uplifts in the Cambrian–Devonian when groundwaters in Vendian rocks were freshened.

The Upper Devonian is marked by accumulation of the Seregovo saliferous formation in the southern Timan region. It should be noted that the Moscow, Pripyat, and Dnepr–Donets basins include Upper Devonian rocks with potash salt deposits, testifying to a higher degree of evaporation concentration of halogenic basins at that time. These basins could be the sources of type III brines confined to underlying aquifers in the eastern part of the syneclise, because they could percolate below the Vendian aquiclude during the Late Devonian tectonomagmatic activation.

Accumulation of salt and formation of gypsum–anhydrite sequences also took place in the Mezen Syneclise in the Early Permian. The downward migration of brines from the bottom of Early Permian halogenic basins produced type II brines that initially filled the entire underlying sedimentary sequence down to the Vendian aquiclude. Type III brines are preserved in the pure form only below the Vendian aquiclude.

The Mesozoic–Cenozoic time is marked by maximum difference of geodynamic regimes in the western and eastern parts of the Mezen Syneclise (Fig. 2b). In the west, uplifts of the territory and hiatuses promoted the denudation of carbonate and gypsum sequences, exhumation of Vendian rocks, intense draining and freshening of groundwaters, and removal of soluble

Table 4. Compositional changes in groundwaters in the upper part of pre-Quaternary rocks in the Severnaya Dvina Basin on the way from recharge to discharge areas

Borehole no.	Rock age	Sampling interval	M, g/l	Unit of measure	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	Ca^{2+}	Mg^{2+}
104	mIII	45	31.3	mg/l	17580	1650	900	9470	200	1500
	mk			mg-eq.l	496	34	15	412	10	123
				mg-eq.%	91	6	3	75	2	23
9·	C_1–Vpd	96–158	2.92	mg/l	535	1260	240	300	495	90
				mg-eq.l	15	26	4	13	25	7
				mg-eq.%	33	58	9	29	55	16
Average			17.1	mg/l	9060	1460	570	4880	350	800
				mg-eq.l	256	30	9	213	17	65
				mg-eq.%	87	10	3	72	6	22
18	Vpd	55–70	17.4	mg/l	9530	1500	120	4350	1280	600
				mg-eq.l	269	31	2	189	64	49
				mg-eq.%	89	10	1	63	21	16
Difference between Borehole 18 and average values				mg/l	+470	+40	–450	–530	+930	–200
				mg-eq.l	+13	+1	–7	–24	+47	–16
				mg-eq.%	+2	0	–2	–9	+15	–6

components from rocks. The composition of groundwaters and rocks was conserved in the eastern part of the Mezen Syneclise.

In the upper Pleistocene, the western part of the Mezen Syneclise was marked by the Boreal transgression of the Mikulino Interglaciation, leading to the accumulation of thick clayey–silty sequences on the coast of the White Sea and in deep paleovalleys, in particular, within the mouth of the Severnaya Dvina River, and salinization of groundwaters in the Vendian Padun Formation. The retreat of the Valdai Glacier 10000 yr ago and formation of recent river valleys again created hydrodynamic conditions favorable for the freshening of groundwaters. However, the salinization was partly retained because of a short duration of the favorable hydrodynamic episode.

FORMATION OF THE COMPOSITION OF WATER AND WATER-ENCLOSING ROCKS

The summary composition of brines and salt waters in the Mezen Syneclise is presented in Tables 3 and 4. The details are given in (Malov, 2001b). The chemical composition of Vendian terrigenous rocks is given in Table 5. This table presents the following data: average values for different formations and the Tamitsa Bed in the eastern part of the syneclise, where the Vendian sequence lies at a maximum depth; average values for different formations and Tamitsa Bed (average for each layer) for the Zolotitsa Uplift area (Fig. 1) in the western part of the syneclise, where the Vendian lies within a depth range of 40–930 m. This is the area of location of the M.V. Lomonosov diamond field. Table 5 also gives average values for different formations and the Tamitsa Bed (average for each layer) for the southeastern shore zone of the White Sea, where the Vendian rocks pinch out and are sampled to a depth of no more than 300 m.

Changes in the average composition of mudstones and sandstones over the Vendian section in the eastern and western parts of the Mezen Syneclise are shown in Figs. 3 and 4. The Padun Formation is characterized by basic differences in almost all parameters. In sandstones of the western area, the silica content increases, while contents of the remaining components decrease. However, the behavior of Fe and, particularly, Na is significantly different in rocks of the Mezen Formation. The Mg distribution in the Vendian sequence also displays a specific pattern.

Na and Ca are the most representative elements for the study area. Figures 3–5 show their distribution in solid phase and solution across the sedimentary sequence in the western and eastern parts of the Mezen Syneclise. The Na and Ca contents in solid phase were calculated on the basis of data from Table 5. Each Vendian formation is characterized by values for mudstones, siltstones, and sandstones (from left to right). The plots show a good correlation between Na contents in solid phase and solution. The irregular Na decrease in the Padun Formation of the Mezen Syneclise is caused by the fact this formation has been represented mainly by Borehole Tsenogorskaya-1 (Fig. 1, 18). As was reported in (Malov, 2001b), this borehole is characterized by anomalously low mineralization in brines of the Padun Formation: TDS 139 g/dm^3, Na 34.8 g/dm^3, and Ca 15.3 g/dm^3) (Fig. 5). However, the

Table 5. Average chemical composition (for each formation and bed) of mudstones, sandstones, and siltstones in the Belomorian–Kuloi Plateau area of the Lomonosov diamond field (BKP), Zimnii Coast of the White Sea and Onega Peninsula (ZC-OP), and the eastern part of the Mezen Syneclise (MS)

Age	Number of determinations			Depth of the bed bottom, m			SiO_2		
	BKP	ZC-OP	MS	BKP	ZC-OP	MS	BKP	ZC-OP	MS
mudstones									
Vpd	1	13	15	200	100	1158–1685	63.8	60.3	62.64
Vmz	21	60	12	450	250	1657–2156	61.15	61.54	63.4
Vup	88	116	40	900	300	1967–4003	62.85	61.06	60.64
sandstones									
Vpd	28	125	2	200	100	1158–1685	91.5	89.78	72.3
Vmz	37	57	11	450	220	1657–2156	78.6	79.38	74.84
Vup	13	6	5	870	270	1700–2061	72.84	79.54	75.22
Vtm	5	2	7	930	300	2181–2554	88.12	87.9	88.92
siltstones									
Vpd	18	44	30	200	100	1158–1685	72	69.79	71.36
Vmz	81	116	5	450	220	1657–2156	66.97	70.43	69.1
Vup	25	55	9	870	270	1700–2061	72.77	68.23	68.12
Vtm	1	1		930	300	2181–2554	88.12		

Age	Al_2O_3			CaO			MgO			Na_2O		
	BKP	ZC-OP	MS	BKP	ZC-OP	MS	BKP	ZC-OP	MS	BKP	ZC-OP	MS
mudstones												
Vpd	16.7	13.74	16.37	0.1	1.25	0.48	1.91	2.26	2.54	0.21	0.15	1.72
Vmz	16.76	16.2	15.12	0.65	1.14	1.13	2.35	2.51	2.31	0.64	0.49	2.11
Vup	15.19	15.73	16.37	0.91	1.27	1.52	2.94	3.14	2.74	1.7	1.5	2.06
sandstones												
Vpd	3.6	4.43	11.14	0.5	0.59	2.6	0.48	0.39	2.14	0.1	0.07	2.28
Vmz	9	9.09	10.46	1.23	1.1	1.31	1.35	1.4	1.67	0.57	0.43	2.7
Vup	10.14	8.74	10.24	2.13	1.3	1.57	2.03	1.4	1.3	1.75	0.9	2.54
Vtm	5.97	6.5	4.38	0.26	0.42	0.35	0.59	0.52	0.47	0.78		1
siltstones												
Vpd	12.8	13.62	12.87	0.48	0.81	0.43	1.24	1.34	1.85	0.14	0.11	1.46
Vmz	14.34	12.51	13.21	0.76	1.31	1.08	1.99	1.87	1.94	0.6	0.62	2.43
Vup	14.81	13.59	13.27	1.46	1.2	1.24	2.68	2.16	2.64	1.8	1.63	2.61
Vtm	11.7			0.3			0.95			1.12		

Age	K_2O			Fe_2O_3			FeO		
	BKP	ZC-OP	MS	BKP	ZC-OP	MS	BKP	ZC-OP	MS
mudstones									
Vpd	4.58	3.43	3.57	7.2	7.04	5.7	0.5	0.47	1.56
Vmz	4.27	4.08	3.08	6.08	6.93	3.75	1.63	1	3.09
Vup	3.29	3.66	3.61	3.39	4.57	3.15	3.16	2.96	3.88
sandstones									
Vpd	1.11	1.01	1.72	1.1	1.78	1.46	0.22	0.44	1.17
Vmz	2.39	2.45	1.73	1.8	2.23	1.75	1.04	0.59	1.74
Vup	1.69	1.8	1.65	1.3	1.1	1.57	2.35	1.26	1.7
Vtm	2.03		1.62	0.54	1.1	0.54	0.33	0.42	1.05
siltstones									
Vpd	2.94	3.5	2.93	5.3	5.63	3.79	0.3	0.36	0.85
Vmz	3.92	3.15	2.67	4.94	3.85	3.61	1.05	0.75	1.73
Vup	3.21	2.96	2.33	3.48	2.67	2.75	3.41	2.3	2.59
Vtm	3.24			2.55			0.15		

Notes: (BKP) Samples taken by PGO Arkhangel'skgeologiya during the geological prospecting for diamonds along structural boreholes 570, 770, 771, 772, 774, 775, 1000, 1000/1, and 200 located in the western part of the Belomorian–Kuloi Plateau in and south of the M.V. Lomonosov diamond field; (ZC) samples taken from Vzl–Vzm rocks down to a depth of approximately 300 m during the geological prospecting in the Zimnii Coast area of the White Sea (Stankovskii *et al.*, 1981); (OP) samples taken from Var-Vtm rocks down to a depth of approximately 190 m during the geological prospecting in the Letnii Coast area of the Onega Peninsula (Kopylov, 1974); (MS) samples taken from structural boreholes in the eastern part of the Mezen Syneclise: Storozhevskaya-1, Tsenogorskaya (Vpd–Vup), Omenskaya-1, Seregovo (Vmz–Vup), and Nizhnyaya Pesha (Vup) (27 analyses along boreholes Storozhevskaya and Seregovo were placed at our disposal by T.A. Babushkin; other analyses were taken from reports of GGP Ukhtaneftegazgeologiya (A.A. Ivanov and B.A. Pimenov) and PGO Arkhangel'skgeologiya).

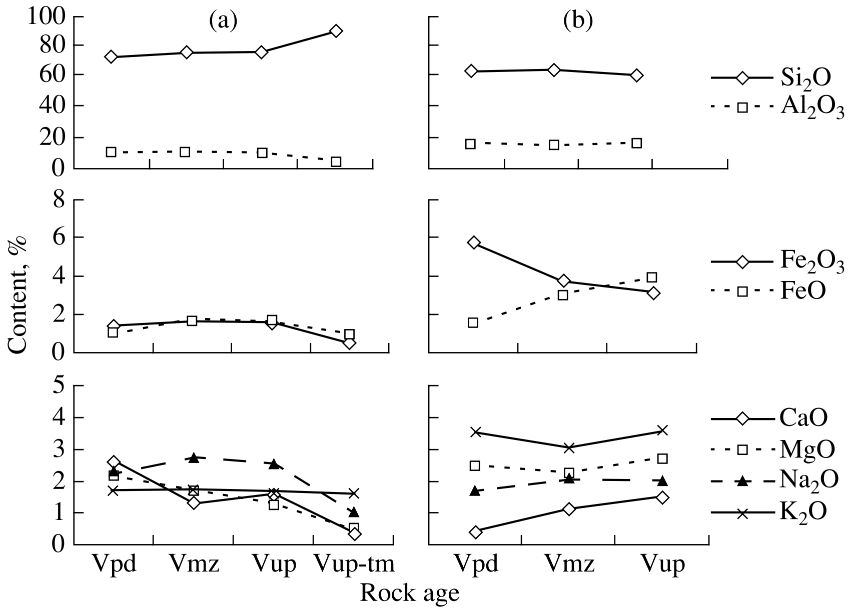

Fig. 3. Changes of average composition (for each formation and bed) of (a) sandstones and (b) mudstones in the area of the M.V. Lomonosov diamond field in the western part of the Belomorian–Kuloi Plateau.

correlation is retained in this case as well. Data points for the Riphean are also based on water composition in Borehole Tsenogorskaya-1 (TDS 205 g/dm^3 against the background value of 270 g/dm^3 in the eastern part of the syneclise). Data points for rocks are adopted from the western part of the syneclise. Therefore, Na contents are also underestimated for the Riphean. These explanations also concern the Ca distribution plots (Fig. 5b). The Ca contents in sandstones of the Padun Formation (average of two results) and Riphean are evidently unrepresentative. The correlation between Ca contents in water and rock is maintained for the eastern part of the syneclise but it lags relative to the Na counterpart in the western part. For example, decrease of the Ca content in water is as much as 15–20 g/dm^3 over the whole sequence, whereas the maximal decrease in rocks (7–15 g/dm^3) is noted only in rocks of the Padun Formation.

The tables and plots presented in this work suggest the following conclusions.

Vendian sediments accumulated in a marine basin with normal salinity. According to (Kotel'nikov and Solodkova, 1993), synthesis of chlorite from pore solutions was the most characteristic process. Subsidence and burial of rocks resulted in the transformation of smectites and kaolinite into hydromicas, as well as significantly reduction of filtration and capacity parameters of rocks (Table 2) owing to the increase of pressure and formation of new minerals.

The composition of rocks related to hypergene processes in the syneclise during the continental hiatus in the Cambrian–Devonian was probably close to that shown in Fig. 3.

In the Late Devonian, the Vendian sedimentary basin located in the eastern part of the Mezen Syneclise was presumably filled with highly concentrated brines (TDS >320 g/dm^3), which consequently produced halite. According to (Malov, 2001b), the composition of brines was as follows (g/dm^3): B ~2, Na 60, Mg 50, K 10, and Ca 0.4. At present, the brine composition recalculated to the TDS content of 320 g/dm^3 is as follows (g/dm^3): B 2, Na 60, Mg 3, K 0.7, and Ca 60. Thus, the brines were depleted in Mg and K (by 47 and 9.3 g/cm^3, respectively) and enriched in Ca (by 59.6 g/dm^3). The Na content practically did not change. Mg and K were extracted from the brines during chloritization and hydromicatization. The principal role in the removal of Ca from rocks was probably played by the hydrolysis of calcium aluminosilicates that are in nonequilibrium state with all types of groundwaters, including brines. In the **VDWE zone** dominated by diffusive mass transfer, these processes follow the mechanism of diffusion kinetics up to the leveling of Ca concentrations in solutions and rocks (Fig. 5b). Parameters of the process were assessed by calculations based on the following formula (Smirnov, 1971):

$$q = 2n_0 C_{av}\sqrt{\frac{Dt}{\pi}},$$

where q is the quantity of salts diffusing through a unit section during time t; C_{av} is the average difference in concentration; D is the coefficient of diffusion; and n_0 is active porosity.

The calculations were carried out for the time of 0.36 Ga. It was accepted that diffusion in a volume of 1 dm^3 mainly occurred via a single effective fracture with an area of 0.1 dm^2. This corresponds to a fracture modulus of 1 fr/2 m core in Vendian terrigenous rocks. We obtained $D = 4 \times 10^{-19}$ m^2/day. If we assume that Ca

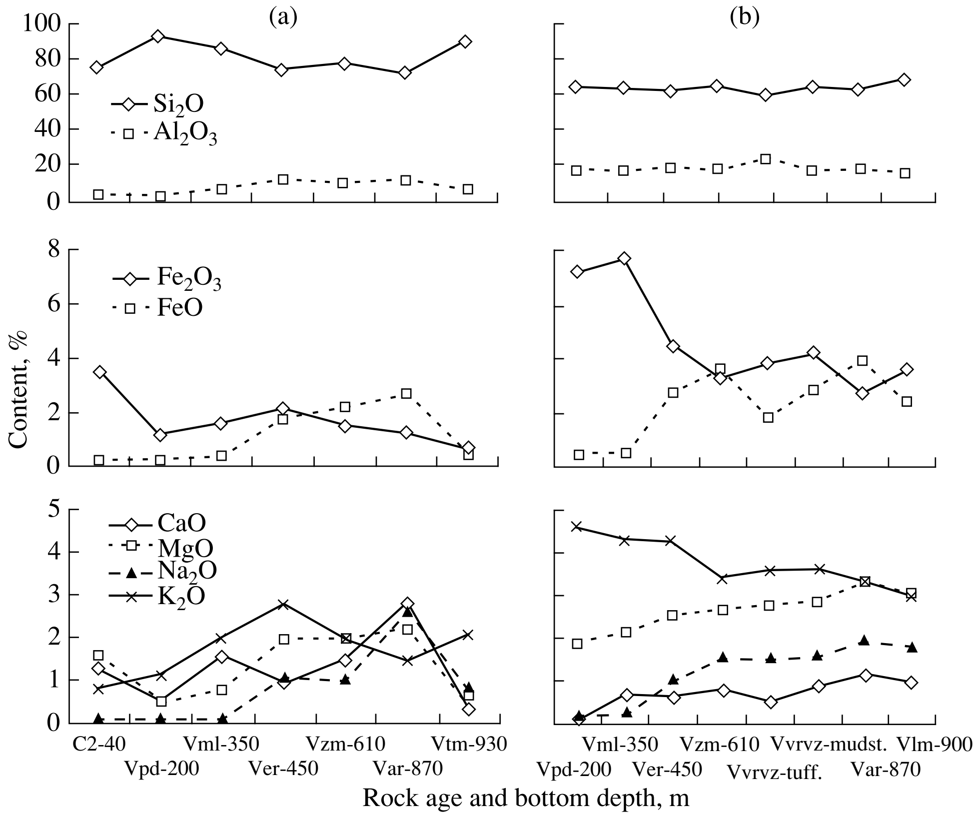

Fig. 4. Changes of average composition (for each formation and bed) of (a) sandstones and (b) mudstones of the Vendian in the eastern part of the Mezen Syneclise.

is delivered to the brine by the diffusion from mineral particles with a size of 0.1 mm in the entire volume of porous space, $D = 2 \times 10^{-30}$ m^2/day.

The calculations suggest that feldspars grains of Vendian terrigenous rocks were partially transformed into clay minerals (up to 10%).

As noted in (Shvartsev, 1991), hydrolysis increases the solution alkalinity subsequently neutralized by carbon dioxide:

$$2CaAl_2Si_2O_8 + 6H_2O$$
$$= Al_4Si_4O_{10}(OH)_8 + 2Ca^{2+} + OH^-,$$

$$CO_2 + OH^- = HCO_3^-.$$

The resultant hydrocarbonate ion binds a part of Ca to form carbonate cement; i.e., the process of dolomitization is also principally possible:

$$2CaCO_3 + MgCl_2(sol)$$
$$\longrightarrow CaCO_3 \cdot MgCO_3 + CaCl_2(sol).$$

During the Late Devonian, the major part of the Mezen Syneclise was characterized by a continental regime with maximum uplift in the kimberlite magmatism area (Malov, 2001a, 2001b, 2002).

In the Middle Carboniferous, the marine basins with normal salinity apparently did not significantly affect the composition of groundwaters and rocks.

Permian halogenic basins were the sources of brines with relatively low Ca content and Cl/Br ratio close to that in seawater (Table 3, type II). Initially, they filled the entire sedimentary cover up to the Vendian aquiclude. The TDS content in brines was as much as 270 g/l. Interaction of brines with rocks resulted in the decrease of Na (from 80 to 60 g/dm^3), Mg (from 12 to 8 mg/dm^3), and K (from 3 to 0.5 g/dm^3), whereas the Ca content increased by 8–10 g/dm^3. Under conditions of convective water exchange in the **DWE zone**, these changes can mainly be related to cation exchange. One cannot also rule out process of dolomitization, hydromicatization, and albitization (Kopeliovich, 1965):

$$2CaAl_2Si_2O_8 + Na^+ + 5H_2O + 3H^+$$
$$\longrightarrow NaAlSi_3O_8 + 2Ca^{2+} + 3Al(OH)_3 + H_4SiO_4.$$

Figure 4 shows an approximate composition of rocks produced by the interaction with Permian brines in the Mezen Syneclise. In the Mesozoic–Cenozoic, the rock composition apparently did not change in the eastern part of the syneclise. In the western part, however, the Vendian sequence was exhumed to the RAWE and AWE zones as a result of stable uplift and subjected to

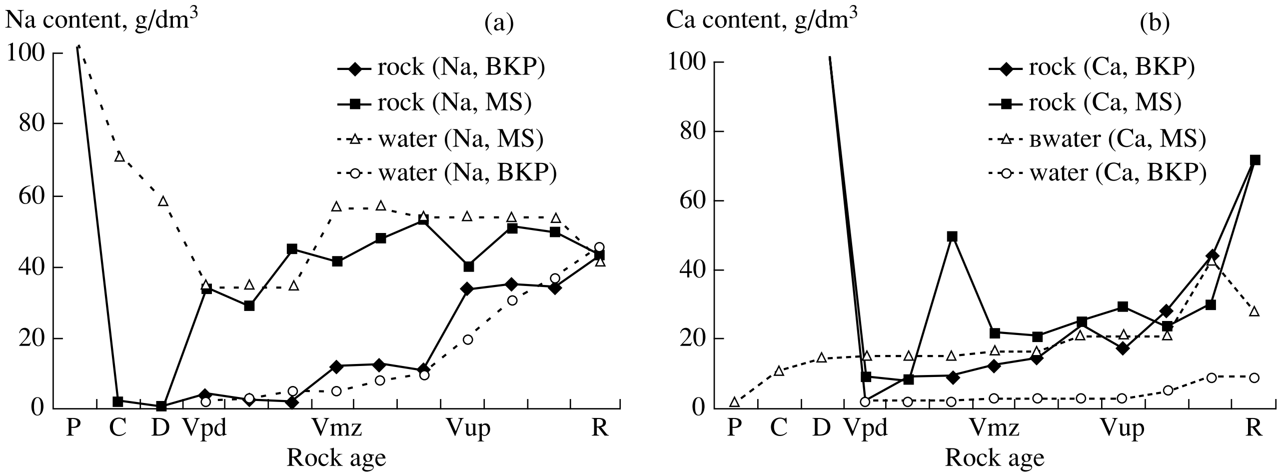

Fig. 5. Contents of (a) Na and (b) Ca in the solid phase and solution vs. rock age. Areas of the M.V. Lomonosov diamond field in the western part of the Belomorian–Kuloi Plateau (BKP) and the eastern part of the Mezen Syneclise (MS).

hypergene weathering down to a depth of approximately 350 m (Fig. 3).

In the **RAWE zone** (down to a depth of 200–600 m), salt waters formed according to the scheme typical of the catchment area of the mouth of the Severnaya Dvina River. Groundwaters in the recharge areas have a fresh Mg–Ca hydrocarbonate composition. As the groundwater percolate along the gypsum-bearing terrigenous rocks on the left bank of the Severnaya Dvina River, they are enriched in Ca and sulfates (due to the dissolution of gypsum) and, to a lesser degree, in Cl and Na derived from pore waters (related to the Devonian–Pleistocene transgression) and hydrolyzed rocks. The waters acquire a Na–Ca chloride-sulfate composition. At the same time, the TDS content in groundwaters increases to 2–3 g/l at a relatively short distance from recharge areas. These waters subsequently mix with sodium chloride waters situated below the thick clays of the Mikulino Interglaciation, resulting in decrease of the TDS content in the sodium chloride waters and changes in their composition (Table 4).

The mixing of waters promotes the increase of Ca and sulfates and the simultaneous decrease of Na and Cl (Table 4, type III). If the content of Ca transferred to solution in the recharge area increases by 7 mg-eq.l, the content of marine sulfates decreases by 4 mg-eq.l. Naturally, this is followed by decrease in the absolute contents of the remaining macrocomponents in groundwaters.

The composition of the "hybrid" groundwater observed in reality (Table 4, row 4) testifies that the mixing of waters is accompanied by the further extraction of Na and Cl (13 mg-eq.l each), dissolution of gypsum and the consequent transfer of Ca and sulfates (1 mg-eq./l each) into the solution, and precipitation of magnesium carbonates and the consequent the removal of hydrocarbonate ion and Mg (7 mg-eq.l each) from the solution. However, the most intense processes are related to substitution of Ca in rocks (46 mg-eq./l) for Na (37 mg-eq./l) and Mg (9 mg-eq./l) dissolved in groundwaters (Table 4).

In the **AWE zone**, fresh waters from siltstones and sandstones of the Padun Formation in the western part of Mezen Syneclise have Mg-Ca hydrocarbonate (TDS content up to 0.2–03 g/l) or sodium hydrocarbonate and sodium chloride-hydrocarbonate compositions (TDS 0.3–0.7 g/l). The water also contains Fe (up to 7.2 mg/l). Chlorine becomes the major anion at a TDS content of 0.9 g/l.

Hence, the most characteristic process is the hydrolysis of sodium aluminosilicates (Zverev, 1982):

$$7NaAlSi_3O_8 + 6H^+ + 20H_2O$$
$$\longrightarrow 3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 10H_4SiO_4^0 + 6Na^+;$$

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O$$
$$\longrightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4^0 + 2Na^+;$$

$$NaAlSi_3O_8 + H^+ + 7H_2O$$
$$\longrightarrow Al(OH)_3 + 3H_4SiO_4^0 + Na^+,$$

and the cation exchange:

$$Ca(HCO_3)_2 + Mg(HCO_3)_2 + CaSO_4 + 6Na(abs)$$
$$\longrightarrow 2Ca(abs) + Mg(abs) + 4NaHCO_3 + Na_2SO_4,$$

which leads to the relative growth of the Na content in groundwaters in accordance with its content in the host rocks (Fig. 5a, BKP).

At the same time, the presence of gypsum inclusions in rocks diminishes the carbonate content in solution:

$$CaSO_4{\cdot}2H_2O + 2NaHCO_3$$
$$\longrightarrow CaCO_3 + NaSO_4 + CO_2 + 3H_2O.$$

In other words, sodium hydrocabonate waters can form in sandy–clayey rocks only under the subdued influence of carbonate and sulfate rocks on water composition.

The lower parts of the fresh water zone are also characterized by the precipitation of calcium carbonates and sulfates. This is accompanied by the formation of carbonate and gypsum cements (Fig. 2a, Vml 350). These processes are related to the denudation of carbonate–sulfate rocks at the surface, infiltration of carbonate and sulfate waters into sedimentary rocks, and their mixing with salt waters:

$$Na_2SO_4 + CaCl_2 + 2H_2O \longrightarrow 2NaCl + CaSO_4 \cdot 2H_2O;$$

$$2NaHCO_3 + CaCl_2 \longrightarrow 2NaCl + CaCO_3 + H_2O + CO_2.$$

These processes are responsible for the lag in the rate of Ca content decrease in the rocks relative to the solution (Fig. 5b, BKP).

CONCLUSIONS

Thus, brines of the VDWE zone in the Mezen Syneclise are characterized by the depletion in Mg (by 47 g/dm^3) and K (by 9.3 g/dm^3) and enrichment in Ca (by 59.6 g/dm^3). The hydrolysis of calcium aluminosilicates probably played a leading role in the removal of Ca from rocks. Brines in the DWE zone are marked by the depletion in Na (from 80 to 60 g/dm^3), Mg (from 12 to 8 g/dm^3), and K (from 3 to 0.5 g/dm^3) and the enrichment in Ca by 8–10 g/dm^3. Under conditions of convective water exchange, these changes may basically be related to the cation exchange. In the RAWE zone, the main processes of cation exchange are the substitution of Ca in rocks (46 mg-eq.l) for Na (37 mg-eq.l) and Mg (9 mg-eq./l), which are dissolved in groundwaters, and the precipitation of calcium carbonates and sulfates. In the AWE zone, the basic processes include the hydrolysis of sodium aluminosilicates and the substitution of Ca, K, and Mg in solutions for Na in rocks.

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