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Article

Study of the Mobilization of Uranium Isotopes in a Sandstone Aquifer Using Methods for the Extraction of Uranium with Different Strength Reagents in Combination with Groundwater Data

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Abstract: A partial extraction procedure was used to study the distribution of uranium in the mineral phases of rocks of an aquifer of sandy-clay deposits of the Vendian in the northwest of Russia. This work is a part of a research project to develop a method for combined radiocarbon and uranium-isotope dating of groundwater. Representative aliquots of each core sample were subjected to five "partial" extractions by treatment with: distilled water, low mineralized fresh natural groundwater, minopolycarboxylic acid chelating agent (0.05M EDTA), 0.5M HCl, 15M HNO_3, and a total digestion, with U isotopes reported in this study for each procedure. The following mineral phases of core samples: adsorbed material, carbonate minerals, amorphous iron oxides, aluminosilicates partial digestion and a crystalline iron oxides, aluminosilicates total digestion and a clay/quartz resistate were characterized. Red-colored siltstones depleted in uranium in relatively readily soluble mineral phases. The concentration of adsorbed uranium was established in the amount of 15.8±2.1 - 30.5±3.9 μg/kg. Carbonate minerals contain even less of this element. In iron hydroxides and the most readily soluble aluminosilicates, its concentrations are in the range 168±24 - 212±28 μg/kg. The most insoluble fraction contains 1.65±0.21 - 4.32±0.45 mg/kg of uranium. In green-colored siltstones, the concentration of adsorbed uranium is much higher: 106±14 - 364±43 μg/kg. Carbonate minerals and amorphous iron oxides contain 1.91±0.21 - 2.34±0.26 mg/kg of uranium. In aluminosilicates and a clay/quartz resistate, uranium concentrations are 5.6±0.5 - 16.8±1.4 mg/kg. Elevated values of ^{234}U:^{238}U activity ratio prevail in the adsorbed material and iron hydroxides. In aluminosilicates and clay/quartz resistate, the values decrease. This indicates the replacement of primary sedimentogenic uranium by secondary hydrogenic uranium adsorbed on the surface of minerals and coprecipitated with iron hydroxides. The results obtained made it possible to carry out preliminary quantitative estimates of the retardation factor and recoil loss factor of uranium in the groundwater of siltstones of the studied Vendian aquifer.

Keywords: Partial extraction, Mineral phases, Uranium, Disequilibrium, Retardation factor

1. Introduction

Uranium isotopes are a powerful tool for refining conceptual models of groundwater [1–4], groundwater dating [5–7] and descriptions of chemical weathering processes [8–10] for up to hundreds of thousands of years [11]. The main initial parameters are i) measured concentration of ^{238}U in the combined solution and solid phase, and ii) measured ^{234}U:^{238}U activity ratio in the

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combined pore fluid and solid phase. They can be obtained by direct measurements in water and rock samples taken in the field.

However, the interpretation of the results is rather complicated. This is due to the heterogeneity of the rocks in their composition. For example, sandy clay sediments of aquifers can contain both poorly soluble grains of quartz and feldspar, as well as soluble carbonate and gypsum cements. Carbonates, iron oxides, and clay minerals are characterized by increased U adsorption on their surfaces [12–14]. Further, daughter nuclides pass most actively into water from surface coatings [15], increasing the ratio of isotope activities in water. In addition, the similarity of the activity ratios of ^{234}U:^{238}U in groundwater and in the most easily leached fractions of water-bearing rocks was noted in the experiments of Lowson et al. [16] , Payne et al. [17], and Dabous et al. [18]. These fractions were defined as adsorbed elements, carbonate minerals and amorphous iron minerals [19]. This may indicate the opposite process: the transition of nonequilibrium nuclides from water to rock with an increase in the ratio of U isotope activities in the rock [20]. Under such conditions, it is difficult to estimate the rate of chemical weathering by using the currently developed methods [21-22].

Therefore, for a more complete understanding of the behavior of uranium isotopes in the water-rock system, a transition from the presentation of solely total concentration and activity data to an additional analysis for finding individual "weak" leach extractants or sequential extractions is necessary. In recent decades, leach data, rather than total decomposition data are widely used in a variety of fields of geoecology (see for example [23-26]). Therefore, in the present work, an attempt is made to use the partial extraction procedure for reconstructing the processes of redistribution of uranium isotopes in certain mineral phases of an aquifer of sandy-clay deposits of the Vendian.

In a previous papers [27-28], the possibility of sharing uranium and carbon isotopes for dating groundwater was discussed. The transport of uranium in solution is reasonably well described with a standard advection-dispersion-exchange formulation:

$$\Delta time = advection + weathering + recoil + desorption + production - precipitation - decay - adsorption$$

[5-7]. Among the many factors, the main ones are t – Groundwater residence time in the aquifer (time), v – Groundwater flow velocity (advection), R_d – Dissolution rate (weathering - precipitation), R – Retardation factor (adsorption - desorption), p – Recoil loss factor (recoil + production), and λ_4 – Decay constants for ^{234}U (decay). Suitable equations were derived by Andrews and Kay [29], Fröhlich and Gellermann [30], Ivanovich et al. [9], and Porcelli [5] to provide a ^{234}U–^{238}U dating method for groundwater under oxidizing conditions. However, the values of R, R_d (a^{-1}) and p needed to be determined. In turn, the recoil loss factor value p depends on the SSA (specific surface area). The published SSA values in sandy aquifers range from 0.9–1.8 $m^2.kg^{-1}$ [31] to 330–390 $m^2.kg^{-1}$ [6]. Accordingly, the ranges of R and R_d can be calculated using these formulas. Therefore, we consider it more appropriate to show R, R_d and p in the form of their ratios: R_d:p (a^{-1}), R:p and R_d:R (a^{-1}) . The main calculated equations are as follows [27]:

$$t = \frac{\ln(k^{-1})}{\lambda_4}, \text{ where } k = 1 - \frac{C_8^{W} \cdot R \cdot (AR_t - 1)}{M_s \cdot C_8^{R} \cdot p} \quad (1)$$

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Where C_8^W is the concentration of uranium in water; C_8^R is the concentration of uranium in the rock; AR_t - $^{234}U/^{238}U$ is the activity ratio in the water sample; M_s is the solid mass to fluid volume ratio.

In this case, two unknown parameters remain in formula (1), which cannot be directly measured in water and rock samples: t and R/p. Therefore, in order to use equation (1), it is necessary to make several determinations of the groundwater age by other methods, for example, using isotopes of carbon. Then, we need to find out whether there is an increase in uranium concentrations in groundwater with a decrease in the concentration of radiocarbon. If this is the case, then the mean values R/p for the studied aquifers are determined. After this, uranium-isotopic dating of other groundwater samples is carried out, which is less labor-intensive and more accessible than radiocarbon dating. The average value of the retardation factor/recoil loss factor ratio (R/p) in samples from the sandstone aquifer of the upper Vendian strata and overlying horizons is assumed to be (24±4) [27].

In this work, it was planned, by determining the amount of uranium adsorbed on the surface of mineral particles, to proceed to a separate assessment of the values of the retardation factor and recoil loss factor of uranium in the groundwater of siltstones of the studied Vendian aquifer.

2. Materials

The borehole GGS2-11 is located in the northwest of Russia at the diamond deposit area (N65°20'48" E41°06'10") and was drilled using a diamond drill bit (92 mm inner diameter, 112 mm outer diameter) and mud rotary methods to 101.2 m below ground surface in July 2018. This core was selected for the present study because the sampled section traverses the aquifer of the Padun formation of the Vendian (Vpd) [27, 28] which is of interest in the present study. For this study, 5 samples were taken from the intervals of 66.7-66.8, 75.2-75.3, 83.9-84, 94-94.1, 99.5-99.6 m (Fig. 1).

The samples were quickly packed in airtight polythene bags. The sample mass collected in each case was about 1500 g. Sub-samples of the material were oven dried at 40 °C for 7 days and homogenized by grinding with an agate mortar and pestle to pass through a 125 μm sieve. The prepared material was stored in glass bottles for sequential extractions and isotopic analyses.

The chemical and mineralogical composition of the Vendian deposits in the area of the diamond deposit was studied in detail during different periods of geological exploration [32-35]. The Padun Formation, 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 a 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, and chlorite. Bitumen and organic carbon are nearly absent. The

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ratio of Fe_2O_3 and FeO forms of iron in "red" siltstones is ~ 17: 1. In "green" siltstones, the Fe_2O_3 content is 2.7 times lower (Table 1).

Figure 1. Photos of samples of studied rocks. 1 - Green siltstones, 66.7-66.8 m. 2 - Red sandstones, 75.2-75.3 m. 3 - Variegated siltstones, 83.9-84 m. 4 - Red siltstones, 94-94.1 m. 5-6 - Green siltstones, 99.5-99.6 m (photo S. Druzhinin)

The description of the samples of the studied rocks was performed on five thin sections of core samples (see Appendix A).

Table 1. The average chemical composition of the red siltstones of the Padun Formation of the Vendian in research area (from 18 determinations) [34] and green siltstones of the sample GGS2-11 (depth 99.5 m), %

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O
[a] RSi	72	12.8	0.48	1.24	0.14	2.94
[b] GSi	74.6	12.5	0.39	1.34	0.16	4.48

	Fe_2O_3	FeO	TiO_2	Cr_2O_3	MnO	P_2O_5	[c] LOI
[a] RSi	5.3	0.3	0.81	0.02	0.14	0.07	3.36
[b] GSi	1.99	0.3	0.91	0.07	0.01	0.11	2.74

[a] RSi - red siltstones. [b] GSi - green siltstones. [c] LOI - loss on ignition.

3. Methods

Representative aliquots of each core sample were subjected to five "partial" extractions and a total digestion, with U isotopes reported in this study for each procedure. The various procedures are described hereinafter.

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3.1. Partial extractions

Distilled water

500 ml distilled water was mixed with 50 g of core sample in centrifuge tubes and shaken for 1 hr on an end-over-end shaker at room temperature. The short duration of the laboratory experiments suggests that dissolution depends upon the ease with which the fine particulates may be freed from the rock surface [36-37]. Firstly, this procedure refers to adsorbed particles.

Low mineralized fresh natural groundwater

500 ml of low mineralized water of Ca-Mg-Na-HCO_3 composition from the borehole had total dissolved solids (TDS) of 285 mg/L (see [28]) and was mixed with 50 g of core sample in centrifuge tubes and shaken for 1 hr on an end-over-end shaker at room temperature. Firstly, adsorbed material was released.

The following four stages were carried out according to the method proposed by Sutherland et al. [26].

0.05M EDTA

Aminopolycarboxylic acid chelating agent (EDTA) at the concentration and pH level used in this study was the weakest extractant after fresh groundwater [26]. As an extractant, EDTA has been widely used in environmental geochemistry. Complexants like EDTA are frequently used to release the readily available (labile) fraction of materials [26]. In our case, this is carbonate cement. The procedure outlined by Singh et al. [38] was followed in this study. 500 mL of 0.05M EDTA (pH 7) was mixed with 50 g of core sample in centrifuge tubes and shaken for 1 hr on an end-over-end shaker at room temperature.

0.5M HCl

According to a review by Sutherland et al. [26], HCl dissolves complexed, adsorbed, precipitated, amorphous or poorly crystallized Fe compounds without significant attack on the crystal lattice. In the present study, 500 mL of 0.5M HCl was mixed with 50 g of core sample and shaken at room temperature for 1 hr on an end-over-end shaker.

15M HNO_3

Nitric acid is an oxidizing agent that is not as powerful in its attack on aluminosilicates as HF, and is thus said to be a partial digestion. Also, crystalline iron oxide is digested by hot HNO_3. In the present study, 500 mL of 15M HNO_3 was mixed with 25 g of core sample and heated for 1 hr while stirring. The resulting solution was evaporated to wet salts, topped up with 500 ml of distilled water and acidified with HCl to pH 1-2.

3.2. Measurements of uranium isotopes after five "partial" extractions

Determinations of uranium isotopes in the resulting solution were made in accordance with Malyshev et al. [39] which is also described in Fröhlich [40]. Spectrometric detection of alpha particles was performed using an alpha spectrometer (PROGRESS-ALPHA, 'DOZE', Russia) with uncertainty of 10-15%. Total error of analysis is defined by $\delta = \delta st + \delta sys$ (statistical + systematic). Measurement uncertainties for U are reported individually (Table 2). Efficiency of ^{232}U extraction was 40-50%.

3.3. Total digestion

Measurements of uranium isotopes were made in accordance with Malyshev et al. [41]. For these analyses, 10 g of core sample was placed in a porcelain crucible and calcined at 500 °C until complete combustion of organic substances. The residue was transferred into a Teflon cup wetted with distilled water. A weighed amount of spiked solution (with known activity of internal standard ^{232}U) was added, followed by 10 cm^3 of 15M HNO_3 and then heated until the reddish brown NO_2 gas vapor disappears. Then after cooling 40 cm^3 of 29M HF and 10 cm^3 of 12M $HClO_4$ were added. The covered Teflon cup was heated until $HClO_4$ vapor appeared. HF treatment was repeated twice; the cup was cooled each time before adding acid and heating until $HClO_4$ fumes were visible. After dissolution and cooling, the edge of the cup and the cover were rinsed with distilled water and the content was transferred to an open Teflon™ dish, where the solution was evaporated again until dense white fumes appeared. This procedure was repeated twice. Finally, the residue was evaporated to give moist salts, which were dissolved in boiling 7M HNO_3 (50 cm^3). The undissolved residue was filtered off and washed three times with 5-10 cm^3 portions of hot 7M HNO_3 and added to the solution. The U solution was transferred to a separatory funnel and a 30%

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solution of freshly purified tributylphosphate in toluene was added to give an aqueous to organic phase ratio of 4:1. Radionuclides were extracted for 5 min. After phase separation, the lower layer was poured back into the beaker. The organic extract was washed twice with an equal volume of 7M HNO_3, then with an equal volume of 0.25M HNO_3 solution in 0.04M HF. The back-extraction of uranium isotopes was performed by washing the organic phase with an equal volume of distilled water three times for 1 min each. The pooled aqueous extracts were evaporated to dryness, treated with 5 cm^3 of concentrated HNO_3 to remove trace organic substances, and evaporated to dryness. The dry residue containing uranium was dissolved in 10 mL of 2% sodium carbonate with heating, then filtered. Dissolved uranium was electrodeposited on polished stainless steel plates for alpha spectrometry.

4. Results

Table 2 and Figs. 2 and 3 show the results of five "partial" extractions and total digestion of the five core samples.

Table 2. Distribution of uranium and measured ^{234}U:^{238}U activity ratios in extracted phases

Solvent	[a] DW	[b] GW	0.05M EDTA	0.5M HCl	15M HNO_3	15M HNO_3 + 12M $HClO_4$ + 29M HF
Substance dissolution, %						
Red siltstones	0.49 – 0.6	0.62 - 1	2.4 – 3.4	1.58 - 2.27	1.82 - 3.42	100
Variegated siltstones	1.04	0.82	1.88	2.3	4.34	100
Green siltstones	0.93 - 1.38	0.64 - 1.93	0.94 - 3.08	2.56 - 6.34	6.85 – 15.4	100
Average	0.89	1	2.34	3.01	6.37	100
U content, µg/kg						
Red siltstones 1	6.2±0.9	15.8±2.1	22.8±3.2	156±23	191±27	4510±467
Red siltstones 2	20±2.6	30.5±3.9	50.3±7.4	103±14	262±34	1910±243
Variegated siltstones	31.6±4.6	30.9±4.1	140±19	230±28	1102±143	5840±578
Green siltstones 1	80±11.1	106±14	857±102	2014±215	5086±512	18800±1504
Green siltstones 2	95.3±11.4	364±43	1860±203	2708±302	3957±415	8328±707
Average	46.6	109	586	1042	2120	7878
U content, %						
Red siltstones	0.14 - 1.1	0.35 - 1.6	0.51 - 2.6	3.5 - 5.4	4.2 - 13.7	100
Variegated siltstones	0.54	0.53	2.4	3.94	18.9	100
Green siltstones	0.43 - 1.14	0.56 - 4.37	4.56 - 22.3	10.7 - 32.5	27.1 - 47.5	100
Average	0.67	1.48	6.47	11.2	22.3	100
^{234}U:^{238}U activity ratio						
Red siltstones	0.97±0.14 - 0.99±0.14	0.96±0.13 - 2.3±0.32	1±0.14 - 1.03±0.14	1.7±0.25 - 2.05±0.29	0.76±0.11 - 1.68±0.22	0.91±0.13 - 1.14±0.16
Variegated siltstones	1.34±0.19	1.68±0.23	1.58±0.21	1.81± 0.24	1.88±0.24	1.12±0.14
Green siltstones	1.87±0.26 - 2.71±0.36	1.65±0.2 - 1.78±0.24	1.39±0.2 - 1.71±0.24	1.03±0.15 - 2.32±0.33	0.98±0.14 - 1.85±0.25	1.12±0.14 - 1.79±0.24
Average	1.58	1.67	1.34	1.78	1.43	1.22

[a] DW - Distilled water. [b] GW – groundwater.

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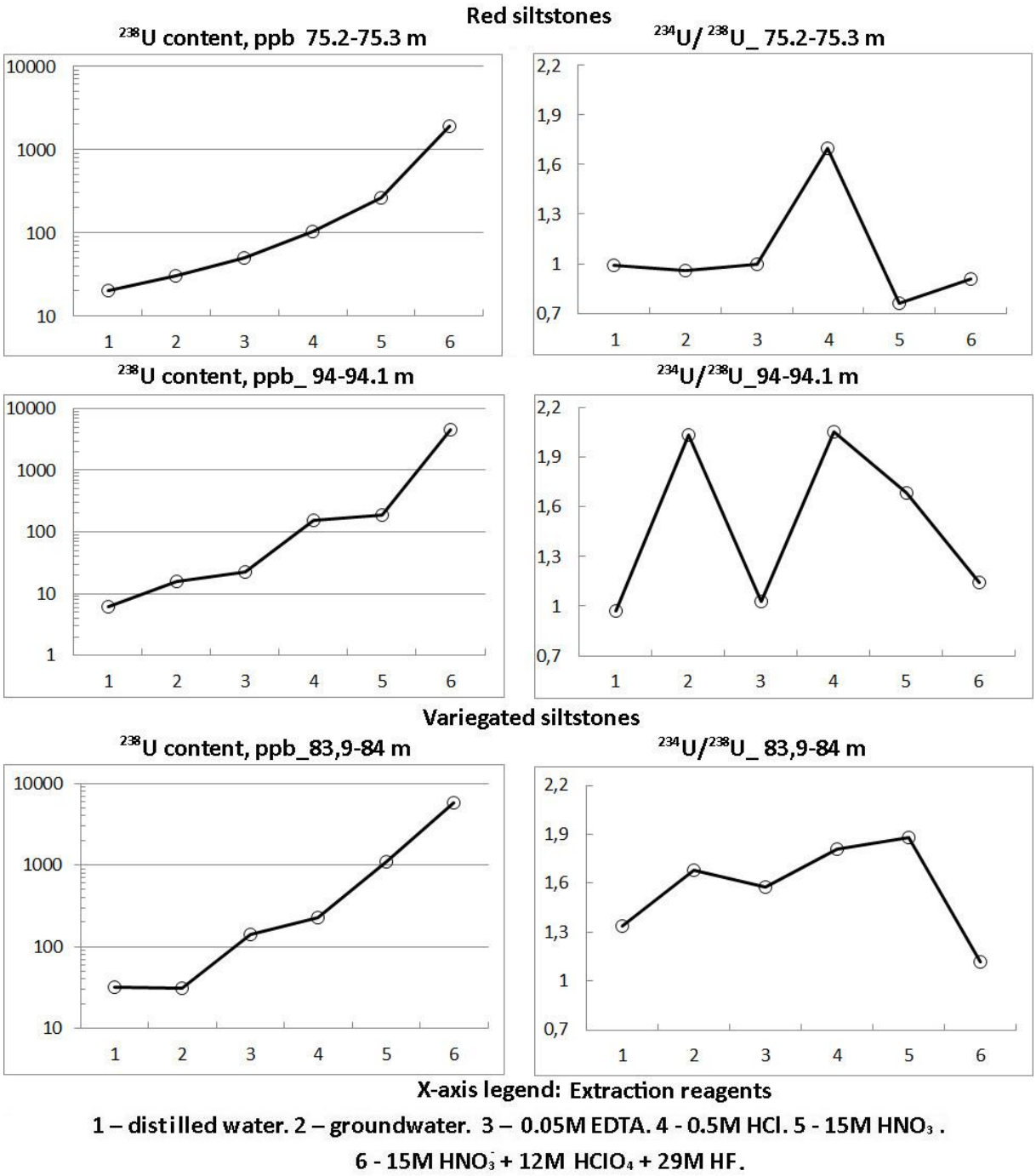

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206 **Figure 2.** Distribution of ^{238}U content and ^{234}U:^{238}U activity ratio in phases 1-6, leached from crushed
207 red and variegated siltstone of Vendian (Ediacaran) Padun Formations

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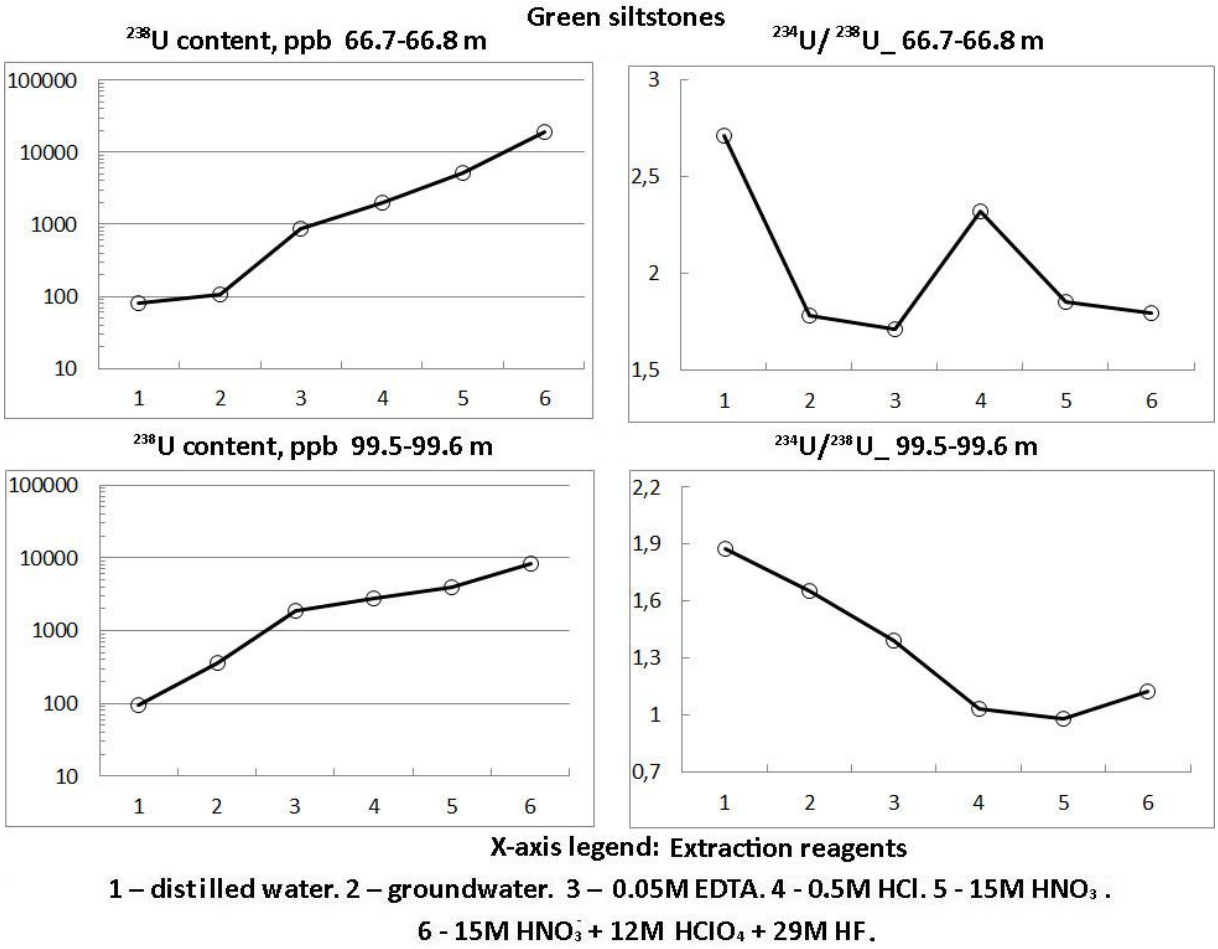

Figure 3. Distribution of ^{238}U content and ^{234}U:^{238}U activity ratio in phases 1-6, leached from crushed green siltstone of Vendian (Ediacaran) Padun Formations

Substance dissolution

As can be seen from Table 2, water dissolved on average about 1% of the samples of siltstones. At the same time, green siltstones dissolved approximately two-fold more intensively. The following solvents, EDTA and 0.5M HCl, are further dissolved in approximately 1% of each. The ratio of red and green siltstones dissolved in hydrochloric acid remains ~ 1:2. The impact of EDTA on both types of rocks is approximately the same. Nitric acid additionally dissolves an average of 3.36% of the rock. Green siltstone dissolves with nitric acid 2.5-fold more intensively than with hydrochloric acid. The bulk of the rock, from 96.58 to 98.18% red siltstones and from 84.6 to 93.15% green siltstones, is dissolved only with a mixture of 15M HNO_3 + 12M $HClO_4$ + 29M HF acids.

Uranium concentration

In red siltstones, the total uranium content was 1910±243 - 4510±467 μg/kg. The material dissolved in groundwater contained 15.8±2.1 - 30.5±3.9 μg/kg. Three subsequent solvents bring the uranium content in the material dissolved by them to 191±27 - 262±34 μg/kg, which is only 4.2 - 13.7% of the total uranium content in red siltstones. The main supply of uranium is contained in these rocks in the highest degree of barely soluble fraction, extractable by complete digestion.

In green siltstones, the total uranium content was 8328±707 - 18800±1504 μg/kg. The material dissolved in groundwater contained 106±14 - 364±43 μg/kg. Three subsequent solvents brought the uranium content in the material dissolved by them to 3957±415 - 5086±512 μg/kg, which is already 27.1 - 47.5% of the total uranium content in green siltstones. The most insoluble fraction, respectively, contained 52.5 - 72.9% of uranium.

^{234}U:^{238}U activity ratio

In red siltstones, the maximum values of ^{234}U:^{238}U activity ratio (1.7±0.25 – 2.3±0.32) were noted in the material dissolved in groundwater and 0.5M HCl. Minimum values (0.76±0.11 – 0.91±0.13) are

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characteristic of the most difficultly soluble 15M HNO_3 and 15M HNO_3 + 12M $HClO_4$ + 29M HF fractions of the studied rocks. In other cases, the values are close to unity.

In green siltstones, one increased value of ^{234}U:^{238}U activity ratio (2.32±0.33) was noted in a material dissolved in 0.5M HCl. Three values close to unity were obtained by dissolving 0.5M HCl, 15M HNO_3 and 15M HNO_3 + 12M $HClO_4$ + 29M HF. However, in the remaining eight experiments, using groundwater, 0.05M EDTA, 15M HNO_3, and 15M HNO_3 + 12M $HClO_4$ + 29M HF as a solvent, the values of ^{234}U:^{238}U activity ratio were high: 1.39±0.2 – 2.71±0.36.

5. Discussion

Substance dissolution

In general, the percentage values of the substance dissolved under the influence of various solvents are approximately consistent with the average chemical composition of siltstones of the Padun Formation of the Vendian in the study area. EDTA, the weakest extractant after fresh groundwater, dissolved up to 3.4% of the substance (Table 2). This corresponds to a loss on ignition (LOI) of 2.74 - 3.36% (Table 1), i.e. the carbonate material of the cement of the studied rocks and other labile fractions. 0.5M HCl additionally dissolved up to 3% of the substance, which is consistent with the content of Fe_2O_3 (2 - 5.3%) in Table 1, that is, it corresponds to amorphous iron oxides. 15M HNO_3 additionally dissolved up to 9% of a substance that can only be represented by the most readily soluble aluminosilicates. A mixture of 15M HNO_3 + 12M $HClO_4$ + 29M HF acids dissolves the remainder of the aluminosilicates and a clay/quartz resistate.

Uranium concentration

Table 3 shows the uranium concentrations converted to mineral phases in μg/kg and %. In red siltstones, the concentrations of adsorbed uranium were established in the amount of 15.8±2.1 - 30.5±3.9 μg/kg. This amounts to 0.35 - 1.6% of its total amount in rocks of this type. Carbonate minerals contain even less uranium: 7±1 – 19.8±2.5 μg/kg. In iron hydroxides and the most readily soluble aluminosilicates, uranium concentrations are in the range 52.7±7.2 - 133±19 and 35±5 - 159±21 μg/kg, respectively. This amounts to a total of 3.7 - 11.1% of its total concentration. The most insoluble fraction contains 1.6±0.2 – 4.3±0.4 mg/kg of uranium. In green siltstones, the concentration of adsorbed uranium is much higher: 106±14 - 364±43 μg/kg (0.56 - 4.37%). The carbonate minerals and amorphous iron oxides contain a total of 1.91±0.21 – 2.34±0.26 mg/kg of uranium (10.15 – 28.2%). In aluminosilicates and a clay/quartz resistate, the concentration of uranium amounts to 5.6±0.5 – 16.8±1.4 mg/kg.

Table 3. Distribution of uranium in the mineral phases.

Defined phases of core samples	Adsorbed elements	Carbonate minerals	Amorphous iron oxides	Aluminosilicates partial digestion and a crystalline iron oxides	Aluminosilicates total digestion and a clay/quartz resistate
U content, μg/kg					
Red siltstones 1	15.8±2.1	7±1	133±19	35±5	4319±447
Red siltstones 2	30.5±3.9	19.8±2.5	52.7±7.2	159±21	1648±210
Variegated siltstones	30.9±4.1	109±15	90±11	873±113	4738±469
Green siltstones 1	106±14	751±89	1157±123	3072±309	13714±1097
Green siltstones 2	364±43	1496±163	848±95	1249±131	4371±371
U content, %					
Red siltstones 1	0.35	0.16	3	0.7	95.8
Red siltstones 2	1.6	1	2.8	8.3	86.3
Variegated siltstones	0.53	1.87	1.54	14.96	81.1
Green siltstones 1	0.56	4	6.15	16.3	72.9
Green siltstones 2	4.37	18	10.2	15	52.5

^{234}U:^{238}U activity ratio

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Increased values of $^{234}U:^{238}U$ activity ratio were noted in the material of red siltstones dissolved in water and 0.5M HCl. That is, uranium isotopes with elevated values of $^{234}U:^{238}U$ activity ratio (greater than 1) were deposited from groundwater on sorbent material and with iron hydroxides. Reduced values of $^{234}U:^{238}U$ activity ratio (less than 1) are characteristic of the most difficultly soluble fractions. In them, the dissolution of uranium by groundwater was practically absent and only depletion of ^{234}U atoms occurred due to recoil loss factor. In green siltstones, there is also a tendency towards a decrease in $^{234}U:^{238}U$ activity ratio in the direction from easily soluble fractions to sparingly soluble fractions (Fig. 3, interval 99.5–99.6 m). However, for a sample taken from the interval 66.7 - 66.8 m, high values of $^{234}U:^{238}U$ activity ratio are observed in all mineral phases. Additional studies are needed to explain this fact.

Evolution of uranium isotopic compositions

The results obtained partially confirm previously expressed ideas about the evolution of U isotopic compositions of the Vendian rock near the study area [20]. It has been established that the processes of chemical weathering of Vendian deposits led to the formation of a strong oxidation zone, developed above 250 m.b.s.l. The inverse correlation between the concentrations of U and Fe (see Tables 1 and 2) in the red siltstones (increased Fe concentrations and reduced U contents) is a result of removal of U in oxidizing conditions, and accumulation of Fe. In red siltstones, the concentration of Fe_2O_3 is 5.3%, and the content of U is 1.9-4.5 mg/kg, in green siltstones the concentration of Fe_2O_3 is 2%, and the content of U is 5.8-18.8 mg/kg. Almost all U in the red siltstones has been replaced by a newly formed "hydrogenic" U (precipitated from groundwater), with an initial $^{234}U:^{238}U$ activity ratio ≈ activity ratio of modern fresh groundwater = 3. The ending of the period of co-precipitation of hydrogenic uranium with iron hydroxide was estimated as 0.9 Ma, which should roughly correspond to the period of a sharp cold snap in the region. After, dissolution and desorption of hydrogenic U occurred during periods with no glaciations and marine transgressions.

Our results are consistent with the experimental results of Lowson et al. [16], Payne et al. [17], and Dabous et al. [18], which note the similarity of the $^{234}U:^{238}U$ activity ratios in groundwater and in the most easily leached fractions of water-bearing rocks.

At the same time, the lower average value of $^{234}U:^{238}U$ activity ratio 0.92 [20] was established in the samples of green siltstones taken in the paleovalley, which was screened by the layer of sea clays. It is explainable by the fact that these deposits have reached a steady state of the $^{234}U:^{238}U$ activity ratio that depends only on their size (the average grain size ≈ 30 μm), because they were under reducing conditions over 1 Ma. A significantly higher content of uranium in them compared to red siltstones shows a considerable variability in the permeability values of the aquifer, whereby they were away from the paths of groundwater filtration and have retained uranium. The green siltstones studied in this work occur in the oxidative conditions of the aquifer which contains young fresh water [28]. They have high concentrations of uranium in readily soluble fractions and high $^{234}U:^{238}U$ activity ratios. This can be explained by their deep processing by groundwater in a relatively recent period (tens - the first hundreds of thousands of years). During this processing, they were in a loose state, as a result of which U was evenly precipitated from water on the surface of disintegrated rock particles in the entire volume of the current green siltstones. Then there was cementation of rocks with Fe hydroxides, carbonates and clay material. After this, the rocks were again compacted under glacial loading. As the second option, it can be assumed that the green siltstones replace lenticular accumulations of organic matter with a high content of U adsorbed from groundwater. The place where 5 samples were taken for this study was the sea shelf of the Mikulinian (Eemian) Sea 115-130 ka ago. Marine sediments up to 50-70 m thick contained a large amount (up to 10%) of organic residues of iodine-containing algae. Organic matter could enter sediments of the upper part of the Vendian Formation during the diagenesis of marine precipitation [42].

Retardation factor

Retardation factor is determined by the formula [43, 6]:

$$R = 1 + M_s \cdot C_8^{\,A} / C_8^{\,W} \qquad (2)$$

where $M_s = \rho_m(1-n)/\rho_{water}n$; $C_8^{\,A}$ - solute concentration of ^{238}U in the stationary solid, μg/kg [44]; $C_8^{\,W}$ - measured concentration of ^{238}U in solution at the point of sampling, μg/kg; ρ_m - mineral density, g/cm^3; ρ_w - pore fluid density, 1 g/cm^3; n - porosity.

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For the study area, the following values of the parameters included in Eq. (2) were previously obtained: C_8^W = 5 μg/kg (from 23 definitions of uranium concentrations in fresh water in a Vendian aquifer [28]; n = 0.23 (from 52 determinations) and ρ_m = 2.75 g/cm³ (from 52 determinations); M_s = 9.2065 [27].

C_8^A can be taken as the average value of U content in adsorbed elements of the red siltstones = 23 μg/kg (Table 3), because green siltstones occupy an insignificant volume in the deposits of the Padun formation of the Vendian compared to red siltstones. However, this value characterizes the entire volume of rock that was crushed before the experiments. Under natural conditions, the movement of water in siltstones and sandstones occurs along pores and cracks, characterized by the value of open porosity. From this open volume, uranium adsorption occurs, which determines the value of the retardation factor. Therefore, as a first approximation, we can take:

$$R = 1 + M_s \cdot C_8^A / C_8^W \cdot n \quad (3)$$

Calculations by the formula (3) give the value of the retardation factor 10.73.

In Malov [27], the average value of the ratio R:p = 24 was determined for a Vendian aquifer, where p is the recoil loss factor. That is, at R = 10.73, the value of p will be 0.45.

The obtained values (10.73 and 0.45) apparently characterize the upper limits of R and p, repectively.

6. Conclusions

The partial extraction procedure was used to reconstruct the redistribution processes of uranium isotopes in certain mineral phases of the aquifer of sandy-clay deposits of the Vendian.

Red siltstones are depleted in uranium in relatively readily soluble mineral phases. The concentration of adsorbed uranium was established as 15.8±2.1 - 30.5±3.9 μg/kg. This accounts for 0.35 - 1.6% of its total amount in rocks of this type. Carbonate minerals contain even less uranium: 7±1 – 19.8±2.5 μg/kg, i.e. 0.16 - 1%. In iron hydroxides and the most readily soluble aluminosilicates, uranium concentrations are in the range 168±24 – 212±28 μg/kg. The most insoluble fraction contains 1.65±0.21 – 4.32±0.45 mg/kg of uranium. In green siltstones, the concentration of adsorbed uranium is much higher: 106±14 - 364±43 μg/kg (0.56 - 4.37%). Carbonate minerals and amorphous iron oxides contain 1.91±0.21 – 2.34±0.26 mg/kg of uranium. In aluminosilicates and a clay/quartz resistate, uranium concentrations are 5.6±0.5 – 16.8±1.4 mg/kg. Such a distribution of uranium in various types of rocks is consistent with the earlier assumption about the removal of uranium from red siltstones in the last 0.9 Ma and its conservation in green siltstones.

Elevated values of ^{234}U:^{238}U activity ratio prevail in the adsorbed material and iron hydroxides. In aluminosilicates and clay/quartz resistate, the values decrease. This indicates the replacement of primary sedimentogenic uranium by secondary hydrogenic uranium adsorbed on the surface of minerals and coprecipitated with iron hydroxides.

The results obtained made it possible to carry out preliminary quantitative estimates of the retardation factor and recoil loss factor of uranium in the groundwater of siltstones of the Vendian aquifer.

At the same time, some uncertainty in the interpretation of the high U contents and high ^{234}U:^{238}U activity ratios in green siltstones obtained in this work should be noted. This requires additional research on a more representative number of samples. Also, the relationship between the extraction solutions and the mineral phases has not yet been precisely established. The mineral phases that were dissolved during the sequential extraction procedure should be examined using X-ray powder diffraction (XRD) analysis and scanning electron microscopy (SEM).

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Appendix A

Description of the thin sections of core samples

Thin sections of core samples (n=5) were prepared in epoxy resin. Thin sections were examined under transmitted, polarized, and reflected light using optical microscopy to determine the minerals and the textural features of the rocks.

1. *Green siltstones 66.7-66.8 m*

The sandy siltstone has a light greenish-gray color. The texture of the rock is heterogeneous, due to the chaotic arrangement of clastic grains and the presence of spots up to 0.4 mm in size with an iron-carbonate aggregate. Clastic material is 70-80% and is represented by grains of quartz, feldspar and quartzite rocks; the composition is dominated by quartz grains. Among feldspars where plagioclases and potassium feldspars are diagnosed, plagioclases prevail. The grain size varies from 0.02 to 0.15 mm; grains up to 0.2 mm in size are rarely found. The surface of the grains is corrosive. Single grains of accessory minerals are noted - tourmaline, ilmenite, epidote, zircon. On separate grains of quartz and feldspar, a regenerative rim is fixed. Some fragments of quartz and feldspar are sericitized. In the rock, single plates of colorless and colored mica up to 0.15-0.25 mm in size are diagnosed; this mica is diagenetic. Film-pore clay-ferruginous cement predominates, and cementation due to regeneration is also fixed. Marks, lenses (not exceeding 0.4-0.5 mm in size) with limonite-goethite and ferruginous-carbonate cement are noted. Carbonate is represented by calcite and it is formed later than limonite-goethite aggregate. Individual detrital grains are partially replaced by a ferruginous carbonate aggregate. Limonite-goethite and carbonate aggregates in cement are epigenetic. Most likely, compaction of sedimentary material, hydromica of cement in siltstone, and a high content of deformed plates are associated with dynamic changes. That is, the structural adjustment of cement is due to the influence of tectonic processes and hydrothermal solutions in the process of formation of kimberlite fields.

2. *Red sandstones 75.2-75.3 m*

Sandstone oligomictic fine-grained silty has brown color with light streaks. Rounded spots 1.0–2.0 mm in size with carbonate cement are fixed in the rock; their location is subparallel. The slanting texture due to particle size distribution is not clearly expressed. In some areas, a random distribution of clastic material is noted. Clastic material is represented by grains of quartz, feldspar and quartzite rocks; the composition is dominated by quartz grains. The size of clastic grains varies from 0.03-0.04 mm to 0.2-0.25 mm. Grain rounding is mostly good and medium. The grain surface is corrosive; regenerative rim is fixed on separate fragments of quartz and feldspar. Separate fragments of quartz and feldspar are sericitized. There are single plates of green mica up to 0.12-0.15 mm in size, which fill individual pores and sometimes partially replace detrital grains. Most likely this mica is epigenetic. Film-pore clay-ferruginous cement predominates, and cementation due to regeneration is also fixed. Spots with limonite-goethite and ferruginous-carbonate cement are noted. Carbonate is represented by calcite and is formed later than limonite-goethite aggregate. Individual detrital grains are partially replaced by a ferruginous carbonate aggregate. Limonite-goethite and carbonate aggregates in cement are epigenetic.

3. *Variegated siltstones 83.9-84 m*

Siltstone with indistinctly expressed oblique and banded textures. Striping does not coincide with layering; alternation of brown and gray, greenish-gray rocks does not form layers. Cross-bedding is due to the presence of argillite microlenses. The composition of this rock does not differ from the sandstones and siltstones that are described in the above.

4. *Red siltstones 94-94.1 m*

Oligomictic siltstone of brown color with indistinctly expressed cross-layered texture. The oblique texture is due to a poorly defined granulometric sorting of clastic material and the presence

of argillite microlenses. Breccia is due to the presence of areas with a random distribution of clastic material, which is associated with sedimentation processes. The presence of sites with limonite-goethite cement is due to epigenetic processes. Clastic material, as in previous thin sections, is represented by grains of quartz, feldspar and quartzite rocks, quartz grains dominate in the composition. The size of clastic grains varies from 0.03-0.04 mm to 0.15-0.2 mm. Grain rounding is mostly average and good. The grain surface is corrosive; a regenerative rim is fixed on separate fragments of quartz and feldspar. Some fragments of quartz and feldspar are sericitized. Rare plates of colorless mica, which are diagenetic, are fixed in this strain. By the nature of the filling, the cement is not continuous, the number of hollow pores is insignificant. Film-pore clay-ferruginous cement predominates, and cementation due to regeneration is also fixed. Spots with limonite-goethite and ferruginous-carbonate cement are noted. Carbonate is represented by calcite and it is later than limonite-goethite aggregate. Limonite-goethite and carbonate aggregates in cement are epigenetic.

5. *Green siltstones 99.5-99.6 m*

Oligomictic siltstone sandy with indistinctly expressed oblique and banded textures. The color of the strain is light greenish gray. In terms of composition and structural-textural features, siltstone does not differ from the rocks that are described in the above.

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