

# Study of the Mobilization of Uranium Isotopes in a Sandstone Aquifer in Combination with Groundwater Data

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Received: 8 November 2019; Accepted: 27 December 2019; Published: 29 December 2019

**Abstract:** This work is part of a research project that aims to develop a method for combined radiocarbon and uranium-isotope dating of groundwater. The specific objective of this study was to investigate the mobility of uranium isotopes in the various mineral phases of rocks of an aquifer of sandy-clay deposits of the Vendian in the northwest of Russia, for which a partial extraction procedure was used. Representative aliquots of each core sample were treated with various reagents: distilled water, low mineralized fresh natural groundwater, minopolycarboxylic acid chelating agent (0.05 M EDTA), 0.5M HCl, 15 M HNO<sub>3</sub>, as well as total digestion, and the U isotope data for each procedure are reported in this study. The following mineral phases of core samples were characterized: sorbed material, carbonate minerals, amorphous iron oxides, partially soluble aluminosilicates and crystalline iron oxides, totally digestible aluminosilicates and a clay/quartz resistate. Red-colored siltstones and sandstones were depleted in uranium in relatively readily soluble mineral phases. The concentration of sorbed uranium was established in the range  $15.8 \pm 2.1$ – $30.5 \pm 3.9$  µg/kg and carbonate minerals contained even less uranium. For iron hydroxides and the most readily soluble aluminosilicates, uranium concentrations were in the range  $168 \pm 24$ – $212 \pm 28$  µg/kg. The most insoluble fraction contained uranium in the range  $1.65 \pm 0.21$ – $4.32 \pm 0.45$  mg/kg. In green-colored siltstones, the concentration of sorbed uranium was much higher in the range  $106 \pm 14$ – $364 \pm 43$  µg/kg. Carbonate minerals and amorphous iron oxides contained uranium in the range  $1.91 \pm 0.21$ – $2.34 \pm 0.26$  mg/kg. In aluminosilicates and a clay/quartz resistate, uranium concentrations were in the range  $5.6 \pm 0.5$ – $16.8 \pm 1.4$  mg/kg. Elevated values of <sup>234</sup>U:<sup>238</sup>U activity ratio prevailed in the sorbed material and iron hydroxides. In aluminosilicates and clay/quartz resistate, the values decreased. This indicates the replacement of primary sedimentogenic uranium by secondary hydrogenic uranium sorbed on the surface of minerals and coprecipitation 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 and sandstones 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 periods of up to hundreds of thousands of years [11]. The main initial parameters are (i) measured concentration of <sup>238</sup>U in the combined solution and solid phase, and (ii) measured <sup>234</sup>U:<sup>238</sup>U activity

ratio in the combined pore fluid and solid phase and they can be obtained by direct measurements in water and rock samples collected in the field.

However, the interpretation of the results is rather complicated due to the compositional heterogeneity of the rocks. 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 sorption on their surfaces [12–14]. Further, daughter nuclides pass most actively into water from surface coatings [15], increasing the uranium isotopes activity ratio in water. In addition, the similarity of the activity ratios of  $^{234}\text{U}$ : $^{238}\text{U}$  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], with the fractions being defined as sorbed elements, carbonate minerals and amorphous iron minerals [19] which could indicate the opposite process which is the transition of nonequilibrium nuclides from water to rock with an increase in the U isotopes activity ratio in the rock [20]. Under such conditions, it is difficult to estimate the rate of chemical weathering and to date natural processes 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 U concentration and U isotopes activity data to an additional analysis using 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 has been 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 previous papers [27,28], the possibility of sharing uranium and carbon isotopes for dating groundwater has been discussed and the transport of uranium in solution is reasonably well described with a standard advection-dispersion-exchange formulation:  $\Delta \text{time} = \text{advection} + \text{weathering} + \text{recoil} + \text{desorption} + \text{production} - \text{precipitation} - \text{decay} - \text{adsorption}$  [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 (sorption - desorption),  $p$ —Recoil loss factor (recoil + production), and  $\lambda_4$ —Decay constants for  $^{234}\text{U}$  (decay). Suitable equations were derived by Andrews and Kay [29], Fröhlich and Gellermann [30], Ivanovich et al. [9], and Porcelli [5] to provide a  $^{234}\text{U}$ – $^{238}\text{U}$  dating method for groundwater under oxidizing conditions. However, the values of  $R$ ,  $R_d$  ( $\text{a}^{-1}$ ) and  $p$  needed to be determined. In turn, the recoil loss factor value  $p$  depends on the specific surface area ( $SSA$ ). The published  $SSA$  values in sandy aquifers range from  $0.9\text{--}1.8 \text{ m}^2 \text{ kg}^{-1}$  [31] to  $330\text{--}390 \text{ m}^2 \text{ kg}^{-1}$  [6]. Accordingly, the ranges of  $R$  and  $R_d$  can be calculated using these formulas. Therefore, we consider it more appropriate to show  $R$  and  $p$  in the form of their ratios:  $R:p$ . The main calculated equations are as follows [27]:

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

where  $C^W$  is the concentration of uranium in water;  $C^R$  is the concentration of uranium in the rock;  $AR_t$ — $^{234}\text{U}$ : $^{238}\text{U}$  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 Equation (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 using other methods such as carbon isotopes. Then, we need to determine 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 can be determined. After this, uranium-isotopic dating of

other groundwater samples, which is less labor-intensive and more accessible than radiocarbon dating, is carried out. The average value of the retardation factor/recoil loss factor ratio ( $R/p$ ) in samples from the siltstone and sandstone aquifer of the upper Vendian strata and overlying horizons is assumed to be  $(24 \pm 4)$  [27].

In the present study, by determining the amount of uranium sorbed on the surface of mineral particles, we planned to proceed to a separate assessment of the values of the retardation factor and recoil loss factor of uranium in the groundwater of siltstones and sandstones of the studied Vendian aquifer.

The Vendian aquifer was selected for this study due to the relatively homogeneous sandy composition of the host sedimentary sediments. In porous reservoirs, the indicators of the behavior of uranium during water-rock interaction are most pronounced. Groundwater is characterized by elevated uranium concentrations and uranium isotope ratios, which is favorable for groundwater dating. Rocks are also characterized by elevated uranium concentrations. The largest roll-type uranium deposits are confined to sandstones. Therefore, traditionally, the dating of groundwater by uranium isotopes was carried out in sandstone aquifers. We also carried out comprehensive isotope-geochemical studies in this direction with the aim of fundamental comprehensive justification of the method of dating groundwater by a complex of isotopes including isotopes of uranium, carbon, hydrogen, and oxygen.

## 2. Materials

The borehole GGS2-11 is located at the diamond deposit area with coordinates N65°20'48" E41°06'10" in the northwest of Russia 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 the ground surface in July 2018. This core was selected 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. Five 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 (Figure 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 in a glove box with nitrogen. The prepared material was stored in glass bottles for sequential extractions and isotopic analyses.

The chemical composition and the mineralogical composition of the Vendian deposits in the area of the diamond deposit were studied in detail during different periods of geological exploration [32–35]. The Padun Formation which is 160 m thick mainly consists of sandstones (60–80%) and siltstones (20–30%) separated by mudstone interlayers. The rocks have a reddish-brown color with pale green lenses and patches and 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 and feldspars, chalcedony, quartzite fragments, biotite, and clayey aggregates are insignificant. The cement has mainly a clayey (hydromicaceous)-ferruginous composition and carbonate and gypsum cements are 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 and the clastic grains consist of quartz (up to 98%), feldspars (up to 10%), and micas (~1%) while 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 ratio of  $\text{Fe}_2\text{O}_3$  and FeO forms of iron in red siltstones is ~ 17: 1 and in green siltstones, the  $\text{Fe}_2\text{O}_3$  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.** Average chemical composition of the red siltstones and sandstones of the Padun Formation of the Vendian in the research area (from 18 determinations) [34] and green siltstones of the sample GGS2-11 (depth 99.5 m), %.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	
<sup>a</sup> RSi	72	12.8	0.48	1.24	0.14	2.94	
<sup>b</sup> GSi	74.6	12.5	0.39	1.34	0.16	4.48	
	Fe <sub>2</sub> O <sub>3</sub>	FeO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	LOI
<sup>a</sup> RSi	5.3	0.3	0.81	0.02	0.14	0.07	3.36
<sup>b</sup> GSi	1.99	0.3	0.91	0.07	0.01	0.11	2.74

<sup>a</sup> RSi—red siltstones and sandstones. <sup>b</sup> GSi—green siltstones. <sup>c</sup> LOI—loss on ignition.

### 3. Methods

Representative aliquots of each core sample were treated with various reagents, with U isotopes being reported in this study for each procedure. The various procedures are described hereinafter.

### 3.1. Partial Extractions

#### 3.1.1. Distilled Water

A volume of 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]. First, this procedure refers to sorbed particles.

#### 3.1.2. Low Mineralized Fresh Natural Groundwater

A volume of 500 mL of low mineralized water of Ca-Mg-Na-HCO<sub>3</sub> 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 h on an end-over-end shaker at room temperature. The boundary conditions when using low-mineralized fresh natural groundwater were as follows: temperature 20 °C, pH 7.7 and redox potential of 230 mV. First, sorbed material was released.

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

#### 3.1.3. 0.05M EDTA

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

#### 3.1.4. 0.5M HCl

According to a review by Sutherland et al. [26], hydrochloric acid (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 h on an end-over-end shaker.

#### 3.1.5. 15M. HNO<sub>3</sub>

Nitric acid (HNO<sub>3</sub>) is an oxidizing agent that is not as powerful in its attack on aluminosilicates as hydrofluoric acid (HF) and is therefore described as a partial digestion. Also, crystalline iron oxide is digested by hot HNO<sub>3</sub>. In the present study, 500 mL of 15 M HNO<sub>3</sub> was mixed with 25 g of core sample and heated for 1 h 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 an uncertainty of 10–15%. Total error of analysis is defined by  $\delta = \delta_{st} + \delta_{sys}$  (statistical + systematic), measurement of uncertainties for U are reported individually (Table 2), and efficiency of <sup>232</sup>U extraction was 40–50%.

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

Solvent	<sup>a</sup> DW	<sup>b</sup> GW	0.05M EDTA	0.5M HCl	15M HNO <sub>3</sub>	15M HNO <sub>3</sub> + 12M HClO <sub>4</sub> + 29M HF
<b>Substance dissolution, %</b>						
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
<b>U content, µg/kg</b>						
Red siltstones	6.2 ± 0.9	15.8 ± 2.1	22.8 ± 3.2	156 ± 23	191 ± 27	4510 ± 467
Red sandstones	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
<b>U content, %</b>						
Red siltstones and sandstones	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
<b><math>^{234}\text{U}</math>:<math>^{238}\text{U}</math> activity ratio</b>						
Red siltstones and sandstones	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

<sup>a</sup> DW—Distilled water, <sup>b</sup> GW—Groundwater.

### 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  $^{232}\text{U}$ ) was added, followed by 10 cm<sup>3</sup> of 15M HNO<sub>3</sub> and this was then heated until the reddish brown NO<sub>2</sub> gas vapor disappeared. Following cooling, 40 cm<sup>3</sup> of 29M HF and 10 cm<sup>3</sup> of 12M HClO<sub>4</sub> were added. The covered Teflon cup was heated until HClO<sub>4</sub> vapor appeared. HF treatment was repeated twice; the cup was cooled each time before adding acid and heating until HClO<sub>4</sub> 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 7 M HNO<sub>3</sub> (50 cm<sup>3</sup>). The undissolved residue was filtered off and washed three times with 5–10 cm<sup>3</sup> portions of hot 7M HNO<sub>3</sub> and added to the solution. The U solution was transferred to a separatory funnel and a 30% 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<sub>3</sub>, then with an equal volume of 0.25M HNO<sub>3</sub> 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<sup>3</sup> of concentrated HNO<sub>3</sub> 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 Figures 2 and 3 show the results of five partial extractions and total digestion of the five core samples.

### 4.1. Substance Dissolution

As can be seen from Table 2, water dissolved on average about 1% of the samples of siltstones and sandstones while green siltstones dissolved approximately two-fold more intensively. The solvents, EDTA and 0.5M HCl, are further dissolved in approximately 1% of each. The ratio of red and green siltstones and sandstones 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 sandstones and from 84.6 to 93.15% green siltstones, is only dissolved with a mixture of 15M HNO<sub>3</sub> + 12M HClO<sub>4</sub> + 29M HF acids.

### 4.2. Uranium Concentration

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

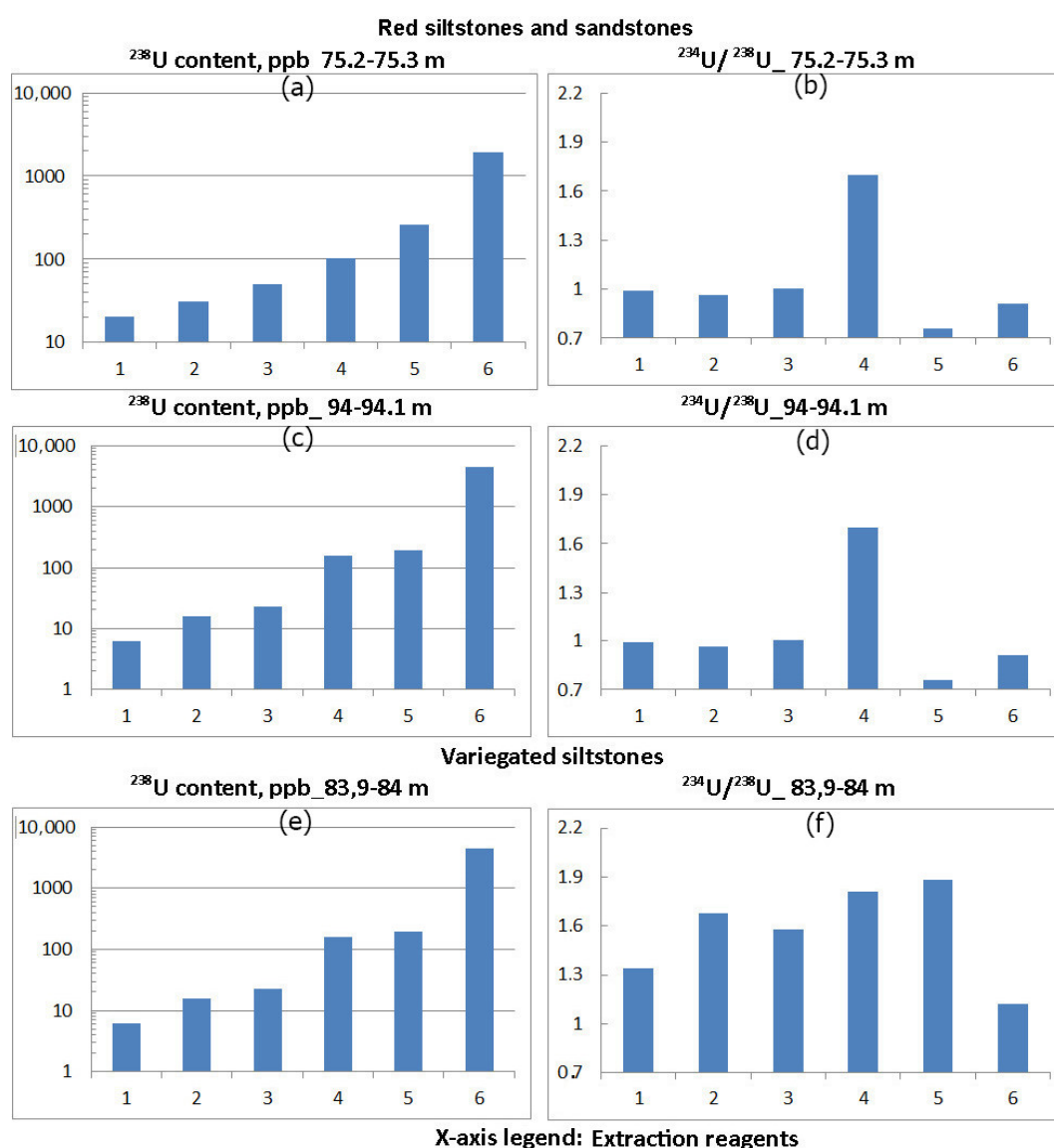
In green siltstones, the total uranium content was  $8328 \pm 707$ – $18,800 \pm 1504$  µg/kg, the material dissolved in groundwater contained  $106 \pm 14$ – $364 \pm 43$  µg/kg, while three subsequent solvents brought the uranium content in the material dissolved by them to  $3957 \pm 415$ – $5086 \pm 512$  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

### 4.3. $^{234}\text{U}$ : $^{238}\text{U}$ Activity Ratio

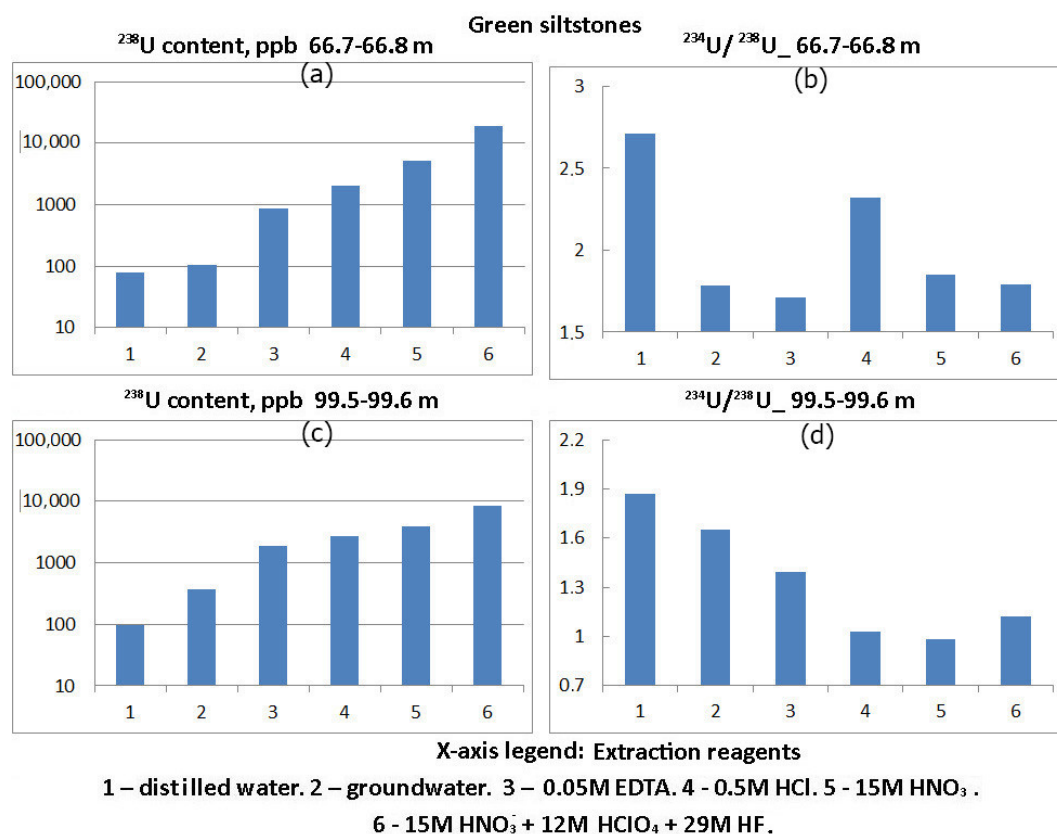
In red siltstones and sandstones, the maximum values of  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratio ( $1.7 \pm 0.25$ – $2.3 \pm 0.32$ ) were noted in the material dissolved in groundwater and 0.5 M HCl. Minimum values ( $0.76 \pm 0.11$ – $0.91 \pm 0.13$ ) are characteristic of the most difficultly soluble 15 M  $\text{HNO}_3$  and 15 M  $\text{HNO}_3$  + 12 M  $\text{HClO}_4$  + 29 M HF fractions of the studied rocks, and in other cases, the values are close to unity.

In green siltstones, one increased value of  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratio ( $2.32 \pm 0.33$ ) was noted in a material dissolved in 0.5 M HCl. Three values close to unity were obtained by dissolving 0.5 M HCl, 15 M  $\text{HNO}_3$  and 15 M  $\text{HNO}_3$  + 12 M  $\text{HClO}_4$  + 29 M HF. However, in the remaining eight experiments using groundwater, 0.05 M EDTA, 15 M  $\text{HNO}_3$ , and 15 M  $\text{HNO}_3$  + 12 M  $\text{HClO}_4$  + 29 M HF as a solvent, the values of  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratio were high:  $1.39 \pm 0.2$ – $2.71 \pm 0.36$ .



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





**Figure 3.** Distribution of  $^{238}\text{U}$  content and  $^{234}\text{U}/^{238}\text{U}$  activity ratio in phases 1–6, leached from crushed green siltstone of Vendian (Ediacaran) Padun Formations.

## 5. Discussion

### 5.1. 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 and sandstones 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. Up to 3% of the substance was additionally dissolved by 0.5 M HCl, which is consistent with the content of  $\text{Fe}_2\text{O}_3$  (2–5.3%) in Table 1, that is, it corresponds to amorphous iron oxides. Up to 9% of a substance that can only be represented by the most readily soluble aluminosilicates was additionally dissolved by 15 M  $\text{HNO}_3$ . A mixture of 15 M  $\text{HNO}_3$  + 12M  $\text{HClO}_4$  + 29 M HF acids dissolved the remainder of the aluminosilicates and a clay/quartz resistate.

### 5.2. Uranium Concentration

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

mg/kg of uranium (10.15–28.2%). In aluminosilicates and a clay/quartz resistate, the concentration of uranium amounts to  $5.6 \pm 0.5$ – $16.8 \pm 1.4$  mg/kg.

**Table 3.** Distribution of uranium in the mineral phases.

Defined Phases of core Samples	Sorbed Elements	Carbonate Minerals and Other Labile Fractions	Amorphous Iron Oxides	Partially Soluble Aluminosilicates and Crystalline Iron Oxides	Totally Digestible Aluminosilicates and a Clay/Quartz Resistate
U content, $\mu\text{g/kg}$					
Red siltstones	$15.8 \pm 2.1$	$7 \pm 1$	$133 \pm 19$	$35 \pm 5$	$4319 \pm 447$
Red sandstones	$30.5 \pm 3.9$	$19.8 \pm 2.5$	$52.7 \pm 7.2$	$159 \pm 21$	$1648 \pm 210$
Variegated siltstones	$30.9 \pm 4.1$	$109 \pm 15$	$90 \pm 11$	$873 \pm 113$	$4738 \pm 469$
Green siltstones 1	$106 \pm 14$	$751 \pm 89$	$1157 \pm 123$	$3072 \pm 309$	$13714 \pm 1097$
Green siltstones 2	$364 \pm 43$	$1496 \pm 163$	$848 \pm 95$	$1249 \pm 131$	$4371 \pm 371$
U content, %					
Red siltstones	0.35	0.16	3	0.7	95.8
Red sandstones	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

### 5.3. $^{234}\text{U}$ : $^{238}\text{U}$ Activity Ratio

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

### 5.4. 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 and sandstones (increased Fe concentrations and reduced U contents) is a result of removal of U in oxidizing conditions, and accumulation of Fe. In red siltstones and sandstones, the concentration of  $\text{Fe}_2\text{O}_3$  is 5.3%, and the content of U is 1.9–4.5 mg/kg, in green siltstones the concentration of  $\text{Fe}_2\text{O}_3$  is 2%, and the content of U is 5.8–18.8 mg/kg. Almost all U in the red siltstones and sandstones has been replaced by a newly formed hydrogenic U (precipitated from groundwater), with an initial  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratio  $\approx$  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 and after that, 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  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratios in groundwater and in the most easily leached fractions of water-bearing rocks.

At the same time, the lower average value of  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratio 0.92 [20] was established in the samples of green siltstones that were collected 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

$^{234}\text{U}$ : $^{238}\text{U}$  activity ratio that depends only on their size (the average grain size  $\approx 30\ \mu\text{m}$ ), because they were under reducing conditions for over 1 Ma. A significantly higher content of uranium in them compared to red siltstones and sandstones 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 that were studied in the present 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  $^{234}\text{U}$ : $^{238}\text{U}$  activity ratios. This can be explained by their deep processing by groundwater in a relatively recent period (tens of thousands to 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 and 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 have entered sediments of the upper part of the Vendian Formation during the diagenesis of marine precipitation [42].

### 5.5. Retardation Factor

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

$$R = 1 + M_s \cdot C^A / C^W \quad (2)$$

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

For the study area, the following values of the parameters included in Equation (2) were previously obtained:  $C^W = 5\ \mu\text{g/kg}$  (from 23 definitions of uranium concentrations in fresh water in a Vendian aquifer [28];  $n = 0.23$  (from 52 determinations) and  $\rho_m = 2.75\ \text{g/cm}^3$  (from 52 determinations);  $M_s = 9.2065$  [27].

$C^A$  can be taken as the average value of U content in adsorbed elements of the red siltstones =  $23\ \mu\text{g/kg}$  (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:

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

Calculations using Equation (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  $p$ , respectively.

## 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 and sandstones are depleted in uranium in relatively readily soluble mineral phases. The concentration of sorbed uranium was established as  $15.8 \pm 2.1$ – $30.5 \pm 3.9$   $\mu\text{g/kg}$ , which accounts for 0.35–1.6% of its total amount in rocks of this type. Carbonate minerals contain even less uranium:  $7 \pm 1$ – $19.8 \pm 2.5$   $\mu\text{g/kg}$ , i.e., 0.16–1% and in iron hydroxides and the most readily soluble aluminosilicates, uranium concentrations are in the range  $168 \pm 24$ – $212 \pm 28$   $\mu\text{g/kg}$  but the most insoluble fraction contains  $1.65 \pm 0.21$ – $4.32 \pm 0.45$  mg/kg of uranium. In green siltstones, the concentration of adsorbed uranium is much higher:  $106 \pm 14$ – $364 \pm 43$   $\mu\text{g/kg}$  (0.56–4.37%), carbonate minerals and amorphous iron oxides contain  $1.91 \pm 0.21$ – $2.34 \pm 0.26$  mg/kg of uranium and in aluminosilicates and a clay/quartz resistate, uranium concentrations are  $5.6 \pm 0.5$ – $16.8 \pm 1.4$  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  $^{234}\text{U}$ : $^{238}\text{U}$  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 and sandstones of the Vendian aquifer. In the future, it is planned to investigate the effect of changes in the boundary conditions ( $t$ , pH, Eh, TDS) of the low mineralized fresh natural groundwater on partial uranium extraction.

At the same time, some uncertainty in the interpretation of the high U contents and high  $^{234}\text{U}$ : $^{238}\text{U}$  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 partial extraction procedure should be examined using X-ray powder diffraction (XRD) analysis and scanning electron microscopy (SEM).

**Author Contributions:** Conceptualization, formal analysis, writing—original draft preparation, A.I.M.; methodology and investigation, S.B.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** This work was supported by the Russian Ministry of Education and Science (project no. № AAAA-A19-119011890018-3), the UB RAS (project no. AAAA-A18-118012390242-5), the Russian Foundation for Basic Research (projects no. 20-05-00045\_A, 18-05-60151\_Arctic; no. 18-05-01041\_A). The authors are grateful to T.N. Markova for the description of the samples of the studied rocks was performed on five thin sections of core samples.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

## 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. Plagioclases prevail among feldspars where plagioclases and potassium feldspars are diagnosed. The grain size varies from 0.02 to 0.15 mm, grains up to 0.2 mm in size are rarely found and 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*

Oligomictic fine-grained silty sandstone 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 has 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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