

VALLE RAIDLA

Chemical and isotope evolution
of groundwater in the Cambrian-Vendian
aquifer system in Estonia



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PRESS

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Supervisors: Prof. Kalle Kirsimäe, Department of Geology,
University of Tartu;

Prof. Rein Vaikmäe, Institute of Geology,
Tallinn University of Technology

Opponent: Prof. Dr. Kristine Walraevens,
University of Gent, Belgium

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS	6
1. INTRODUCTION	7
2. THEORETICAL BACKGROUND	9
3. GEOLOGY AND HYDROGEOLOGY OF THE CAMBRIAN- VENDIAN AQUIFER SYSTEM	13
4. MATERIAL AND METHODS	16
5. RESULTS AND DISCUSSION	19
5.1. Aquifer matrix	19
5.2. Groundwater mixing and dilution	21
5.3. Carbon and sulphate system of groundwater	24
5.4. ¹⁴ C age and evolution of groundwater in the Cambrian–Vendian aquifer system	27
6. CONCLUSIONS	31
ACKNOWLEDGEMENTS	33
REFERENCES	34
SUMMARY IN ESTONIAN	38
PAPERS I–IV	41
CURRICULUM VITAE	129
ELULOOKIRJELDUS.....	131

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers, which are referred to in the text by their Roman numerals. The papers are reprinted by kind permission of the publishers.

- I Raidla V., Kirsimäe K., Vaikmäe R., Jõelet A., Karro E., Marandi A., Savitskaja L. 2009. Geochemical evolution of groundwater in the Cambrian-Vendian aquifer system of the Baltic Basin. *Chemical Geology*, 219–231.

- II Raidla V., Kaup E., Knöeller K., Martma T., Vaikmäe R., Kirsimäe K. Carbon and sulphur isotope systematics of the Cambrian-Vendian aquifer in the northern Baltic Basin: implications to the age and evolution of groundwater. Submitted manuscript.

- III Vaikmäe R., Kaup E., Marandi A., Martma T., Raidla V., Vallner L. 2008. The Cambrian-Vendian aquifer, Estonia. Edmunds, W.M. and Shand, P. (Eds.). *The natural baseline quality of groundwater*. Blackwell Publishing, 353–371.

- IV Raidla V., Kirsimäe K., Bitjukova L., Jõelet A., Shogenova A., Šliaupa S. 2006. Lithology and diagenesis of the poorly consolidated Cambrian siliciclastic sediments in the northern Baltic Sedimentary Basin. *Geological Quarterly*, 50, 395–406.

Author's contribution

Paper I: The author was responsible for fieldwork, data analysis and interpretation, and the writing of the manuscript.

Paper II: The author was responsible for fieldwork, radiocarbon measurements, data interpretation, and the writing of the manuscript.

Paper III: The author was responsible for fieldwork, and contributed to the writing of the manuscript.

Paper IV: The author's contribution involves data analysis, interpretation of the results, and the writing of the manuscript.

I. INTRODUCTION

Cambrian-Vendian aquifer system is a confined water-body found in the Baltic Basin, the western and north-western part of the East-European Platform. The groundwater in the deeply buried parts of the aquifer (depth >1000 m) is a typical Na-Ca-Cl basinal brine (formation water) with salinity (total dissolved solids – TDS) of >1000 mg·l⁻¹. However, in shallowly buried marginal areas of the aquifer, particularly in northern part of the Baltic Basin where the aquifer forming rocks outcrop to the surface, the water is fresh (TDS <1000 mg·l⁻¹), drinkable, and used in the public water supply. The fresh water at the northern margin of the Cambrian-Vendian aquifer has an unusual stable isotope composition of depleted δ¹⁸O in the range between –18 to –22 ‰ VSMOW, whereas the isotopic composition of the present day precipitation is only –8 to –11 ‰ VSMOW (Punning et. al 1987, Vaikmäe et al. 2008 – PAPER III). The depleted δ¹⁸O composition indicates glacial origin of the freshened groundwater. Replacement of saline Na-Ca-Cl basinal brines with fresh and isotopically depleted glacial meltwater recharge has been extensively reported on the Canadian Shield (e.g. Douglas et al. 2000) and in its marginal intercratonic sedimentary basins – Forest City, Illinois, Michigan and Appalachian Basins (e.g. Siegel and Mandle 1984, Long et al. 1988, Siegel 1989, Grasby and Betcher 2002, McIntosh and Walter, 2005, 2006) that were repeatedly glaciated by the Laurentide ice sheet during the Pleistocene.

Similarly, the Baltic Basin was repeatedly covered by Scandinavian glaciers that reached the maximum thickness of about 1,000–2,500 meters in northern part of the basin (Fjeldskaar 1989, Denton and Huges 1981). Punning et al. (1987) and Vaikmäe et al. (2001) suggested that the glacial meltwater with a more negative δ¹⁸O composition intruded into Cambrian-Vendian aquifer under the elevated hydrostatic head of the Scandinavian continental ice during the last Ice Age, but the time and mechanism of the recharge of glacial waters are still poorly understood. Yezhova et al. (1996) suggested that an intrusion of surficial glacial meltwaters from Late Glacial Baltic Ice Lake occurred after the continental ice had retreated. However, the measured ¹⁴C activities (1.4 – 6.8 pmc) of the Cambrian-Vendian groundwater indicate that the average age of the groundwater varies between 15,000 – 35,000 BP, which suggests that the meltwater intrusion took place much earlier, whilst the Estonian territory was covered by an ice sheet (Vaikmäe et al. 2001). It was assumed that the intrusion of the water occurred through the aquifer's outcrop area in North-Estonia (Jõelet 1998), or by infiltration of subglacial drainage through the tunnel-valleys during the Late Weichselian (Vaikmäe et al. 2001). Alternatively, Mokrik (1997) suggested that the depleted stable isotope composition of oxygen in the Cambrian-Vendian groundwater resulted from cryogenic metamorphism of shallow water under permafrost conditions (e.g. Lacelle et al. 2006).

Clark and Fritz (1997) and Geyh (2000) have shown that traditional ¹⁴C-age calculation methods may not be appropriate for converting ¹⁴C-activity of the water into realistic age. This results from uncertainties in the carbon cycle of the

groundwater, which is controlled by several processes, such as dissolution of carbonate minerals and isotope exchange between water and the rock matrix of the aquifer. These processes cause progressive mixing/dilution of radiocarbon and the old carbon of the aquifer. Moreover, old carbon is added to the groundwater by methane oxidation and degradation of (old) organic carbon in aquifer sediments (Aravena et al. 2003, Herczeg et al. 1991, van Stempvoort 2005).

Since 1960s, scientists have tried to develop models allowing to transform conventional radiocarbon age to true radiocarbon age. Most of the radiocarbon correction models have been developed for simple homogenous systems, where a single predominant geochemical process is assumed to have influenced ^{14}C concentrations in the groundwater. In nature, however, such simple systems are rare. Usually, the rock composition of an aquifer is variable and there are several geochemical processes influencing the preliminary ^{14}C age of the groundwater. Therefore, it is necessary to develop a geochemical mass balance model to estimate the compliance of the calculated results to the real natural conditions, and, consequently, determine the most important natural processes, which have influenced the formation of carbon's isotope composition.

This thesis studies the chemical and stable isotope composition, and the ^{14}C age of the groundwater of the Cambrian-Vendian aquifer in the Baltic Basin at its northern margin. The aims of the thesis are:

- 1) to reveal the factors controlling the geochemistry of the aquifer's water,
- 2) to elaborate the mass-balance model of the carbonate system for modelling the groundwater residence age in the Cambrian-Vendian aquifer system, and,
- 3) based on the results obtained, to estimate the conditions of glacial meltwater infiltration.

2. THEORETICAL BACKGROUND

Tracing groundwater by means of environmental isotopes offers unique and supplementary information on the origin and movement of groundwater and its dissolved constituents, as well as allows a quantitative evaluation of mixing and other physical processes influencing the groundwater. To understand geochemical processes in groundwater an understanding of chemical and isotopic composition of the rock (aquifer matrix) is required. Isotopic and chemical composition of groundwater reflects the mineralogical composition of the rocks in the aquifer, and can be used to localise recharge areas as well as determine the origin of groundwater (meteoric, marine, fossil, magmatic, or metamorphic water) and of individual chemical components (e.g. carbonate, sulphate, nitrate and ammonium) (Appelo and Postma 1999, Drever 2002). The composition of water can also give information about processes of water-rock interaction and microbial processes in the water, which also modify the $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (Clark and Fritz 1997).

In a natural hydrological cycle the fractionation of isotopes with different mass numbers occurs. Changes in ratio of oxygen isotopes ^{18}O and ^{16}O of water molecules reflect variations in evaporation and precipitation accumulation in glaciers, atmosphere, groundwater, and other large water reservoirs. Therefore, $\delta^{18}\text{O}$ is a valuable tool for establishing the possible origin of waters and for estimating the conditions in which they were formed. Mixing within a regional groundwater flow system has the effect of averaging the isotopic composition of various groundwaters from different recharge environments. The simplest natural chemical tracing of groundwater movement relies on measuring the chloride concentration. Chlorine (Cl^-) is a conservative tracer, which is subject to neither adsorption nor desorption during transport. Hence, the relation between chloride concentration and $\delta^{18}\text{O}$ values illustrates the effect of various processes, such as groundwater mixing, dissolution of halite or admixture of saline water, seawater or brine (Clark and Fritz 1997, Turner and Barnes 2006).

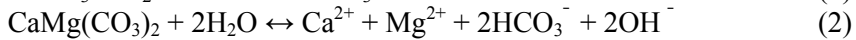
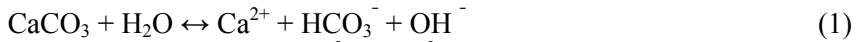
Similarly to oxygen isotopes, carbon isotopes ^{12}C and ^{13}C behave somewhat differently in carbon cycles as well, depending on differences in their masses, which causes fractionation. Great differences in $\delta^{13}\text{C}$ concentrations may occur between carbon reservoirs. This makes $\delta^{13}\text{C}$ a perfect tracer for studying carbon cycles. The isotopic composition of carbon in the dissolved carbon constituents of groundwater is quite variable. The sources of carbon dissolved in groundwater are soil CO_2 , CO_2 of geogenic origin, magmatic CO_2 (from deep crustal or mantle sources), or, in fluid inclusions, organic matter in soils and rocks, methane, and carbonate minerals. Each of these sources has a different carbon isotopic composition contributing to the total dissolved carbon in various proportions. Therefore, the isotopic composition of dissolved inorganic carbon compounds in groundwater has a wide range of $\delta^{13}\text{C}$ values (Geyh and Schleicher 1990, Clark and Fritz 1997).

Radioactive carbon isotope ^{14}C is used for studying natural processes, in order to give them a temporal dimension. Dating groundwater by using the ^{14}C

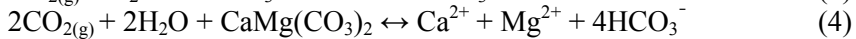
method does not attempt to establish the exact formation time of water molecules, but tries to determine when the water was last in contact with the atmosphere and obtained carbon dioxide containing radioactive carbon. Therefore, it is not correct to use the term “absolute age”, but the term “conventional age” should be preferred denoting the period during which the water has been circling in the basin under study (Geyh 2000, Clark and Fritz 1997).

Radiocarbon does not behave as a conservative tracer in groundwater as it is a constituent of the dissolved inorganic carbon (DIC) compounds undergoing hydrochemical reactions with the rock matrix of the host aquifer. Quantification of groundwater residence time requires correction for additions of non-atmospheric carbon. Numerous approaches to this problem have been attempted, including simple empirical measurements (Vogel 1970), simplified chemical equilibrium mass balance (Tamers 1975), mass balance using $\delta^{13}\text{C}$ as an analogue for ^{14}C (Ingerson and Pearson 1964), and combined chemical/ $\delta^{13}\text{C}$ mass balance (Fontes and Garnier 1979, Mook 1980). In other cases, the isotopic composition of carbon may be strongly altered by numerous surface reactions, which are difficult to quantify, and interpretations may be speculative, at best. Interpretations must be evaluated on a case-by-case basis, keeping in mind that only model age can be calculated and the reliability of this will depend on how well the carbon cycle in an individual aquifer is understood.

During infiltration to the soil the water can pass through carbonate rocks (or carbonate mineral rich rocks and sediments), the dissolution of which adds more carbon to the groundwater. In pure water the dissolution intensity of carbonates is low and does not explain the high concentration of dissolved carbonate in many natural groundwaters.



In most groundwater systems carbonate dissolution is accelerated by carbonic acid formed from the CO_2 dissolved from the atmosphere:



Dissolution of carbonates (mainly calcite and dolomite), according to these reactions, is controlled by partial pressure of CO_2 . Therefore, the release of carbon originating from carbonate rocks is influenced by mass exchange between groundwater and surface atmosphere. In an open system, calcite dissolution occurs at a constant CO_2 concentration, because there is an unsaturated zone where gas and liquid phases co-exist (Clark and Fritz 1997). Since groundwater's CO_2 is constantly fed by CO_2 of the ground's atmosphere, favourable conditions for carbonate dissolution are created and DIC concentration can be high (Appelo and Postma 1999).

In a closed system, the groundwater infiltrates through the soil and before it meets carbonate rocks it has already been isolated from the surface atmosphere. In this case, the groundwater will retain its CO₂ concentration fixed in the soil and will not be fed by dissolution of carbonates. DIC concentration in the groundwater remains low. Dissolution of carbonates under closed conditions is characteristic of recharge areas, where infiltration to the aquifer is fast (e.g. in karst), and in the soil, where the carbonate content is low or lacking completely (Clark and Fritz 1997, Appelo and Postma 1999, Geyh and Schleicher 1990). However, the partly open systems are more common, where calcite dissolution begins in an open system, which develops during infiltration gradually into a closed system in deeper parts of the section.

The $\delta^{13}\text{C}_{\text{DIC}}$ of water obtained during carbonate mineral dissolution depends both on the geochemical openness of the groundwater system and the stable isotope composition of the rocks in the aquifer. In a carbonate free siliciclastic rock the $\delta^{13}\text{C}$ composition of groundwater does not differ considerably from the $\delta^{13}\text{C}$ composition of the surface atmosphere (–7 to –8‰), but calcite or dolomite dissolution in a soil rich in carbonate minerals could considerably influence the groundwater's $\delta^{13}\text{C}_{\text{DIC}}$. $\delta^{13}\text{C}$ values of carbonates are generally close to 0‰, causing widespread enrichment in groundwater's $\delta^{13}\text{C}_{\text{DIC}}$ (Clark and Fritz 1997, Fontes 1983)

When dissolution occurs in a completely open system, the $\delta^{13}\text{C}$ is controlled by CO₂ of the soil, since it has a much bigger reservoir compared to groundwater in a zone unsaturated by DIC. When dissolution occurs in a completely closed system, $\delta^{13}\text{C}$ originating from carbonate minerals becomes predominant in DIC (Clark and Fritz 1997, Geyh and Schleicher 1990).

Chemical interaction between groundwater and organic matter has an important influence on the carbon isotope composition of the dissolved inorganic carbon compounds in groundwater. Microbial communities in groundwater can use alternative metabolic strategies to oxidize either natural organic compounds or organic contaminants, such as hydrocarbons. Typically, oxygen is the favored electron acceptor, followed by nitrate, Mn^{4+,3+}, Fe³⁺, sulphate, and, finally, methanogenesis (Appelo and Postma 1999, Chapelle 2001). In groundwater, the most common reaction pathway is the reduction of CO₂ by using molecular H₂. The process can be expressed as a series of simplified reactions involving CO₂ and H₂ production by fermentative bacteria followed by the formation of CH₄ by methanogens (Clark and Fritz 1997):



The process has a strong effect on $\delta^{13}\text{C}$, mainly through the CO₂ reduction step, which causes significant carbon isotope fractionation (Clark and Fritz 1997, Geyh 2000).

Stable isotope ratios of sulphate are strongly affected by isotopic fractionation caused by microbial activity as well as water-rock interactions. During bacterial sulphate reduction the residual sulphate becomes enriched in

$\delta^{34}\text{S}$, since the lighter ^{32}S isotope is preferentially incorporated into the H_2S reaction product. Bacterially mediated equilibration processes may concentrate ^{18}O in the residual sulphate (Mizutani and Rafter 1973, Strebel et al. 1990).

During hydrochemical evolution the concentration of individual ionic species increases, remains constant, or decreases. In water-rock interaction a Na^+ increase along the aquifer flowpath, associated with a decrease in Ca^{2+} and Mg^{2+} , is attributed to ion exchange with clay minerals (Toran and Saunders 1999, Drever 2002, Appelo and Postma 1999). These processes do not affect the radiocarbon activity directly, but may remarkably change the background data, which are used in the radiocarbon age correcting models.

3. GEOLOGY AND HYDROGEOLOGY OF THE CAMBRIAN-VENDIAN AQUIFER SYSTEM

The Cambrian–Vendian aquifer system is found in the Baltic Basin – Estonia, northwestern Russia, Latvia, and Lithuania (Figure 1). The aquifer system consists of tectonically undisturbed Cambrian–Ediacaran alternating marine sandstone–siltstone–claystone sedimentary formations, which lie on the peneplain of the crystalline basement of the Precambrian Fennoscandian Shield. The crystalline basement and sedimentary formation including the aquifer are gradually sloping by $2\text{--}4\text{ m}\cdot\text{km}^{-1}$ towards the south. Along the southern coast of the Gulf of Finland (North-Estonian coastline) the aquifer lies at 60–70 m depth. Its depth from the surface increases to 150–300 m in Central-Estonia, 450–600 m in South Estonia and $>700\text{ m}$ in northern Latvia and Russia (Figure 1). The thickness of the aquifer decreases from 80–90 meters in northeast Estonia to only few meters in West-Estonian islands, disappearing entirely in South-Estonia (Figure 1). The Ediacaran sediments are missing in West- and South-Estonia, but are extensive in eastern Latvia, Lithuania and north-western Russia. The aquifer system recharges in the southern Estonia, in the Haanja and Otepää heights and the discharge occurs towards the depressions of the Baltic Sea and the Gulf of Finland. The estimated velocities of deep groundwater movement are between 10^{-4} and $10^{-3}\text{ m}\cdot\text{d}^{-1}$ (Perens and Vallner 1997). The water is under pressure and the aquifer is confined between the underlying crystalline basement of the Palaeoproterozoic age and the overlying Lükati-Lontova aquitard. The crystalline basement comprises mainly of gneisses and biotite gneisses (Koistinen et al. 1996), and its upper part is fractured and weathered.

The Lükati-Lontova aquitard is composed of silty clays, siltstones and clays of the Lower-Cambrian age. The thickness of the clayey complex is 90–100 meters in North-Estonia, but decreases towards the south until disappearing at the Lokno-Mõniste structural uplift in South-Estonia. The aquitard has a strong isolation capacity with vertical hydraulic conductivity of $10^{-7}\text{--}10^{-5}\text{ m}\cdot\text{d}^{-1}$. The Lükati-Lontova clays are westwards gradually replaced by interbedded clay and sandstone of the Voosi Formation, the isolation capacity of which is less compared with Lontova-Lükati clays (hydraulic conductivity $>10^{-5}\text{ m}\cdot\text{d}^{-1}$) (Perens and Vallner 1997).

At its northernmost margin, the aquitard and the water-bearing bedrock formation are penetrated by a dense set of buried valleys filled, in their lower parts, with loamy till and glaciofluvial gravel (Tavast 1997). The valleys serve as recharge areas through which the water from the upper groundwater horizons infiltrates to the Cambrian-Vendian aquifer system. They are oriented approximately perpendicularly to the north Estonian coastline (Figure 1). In northern and central Estonia, the siliciclastic rocks of the Cambrian-Vendian aquifer are in the most part of the area covered by up to 500 m thick Ordovician and Silurian marine carbonate rocks.

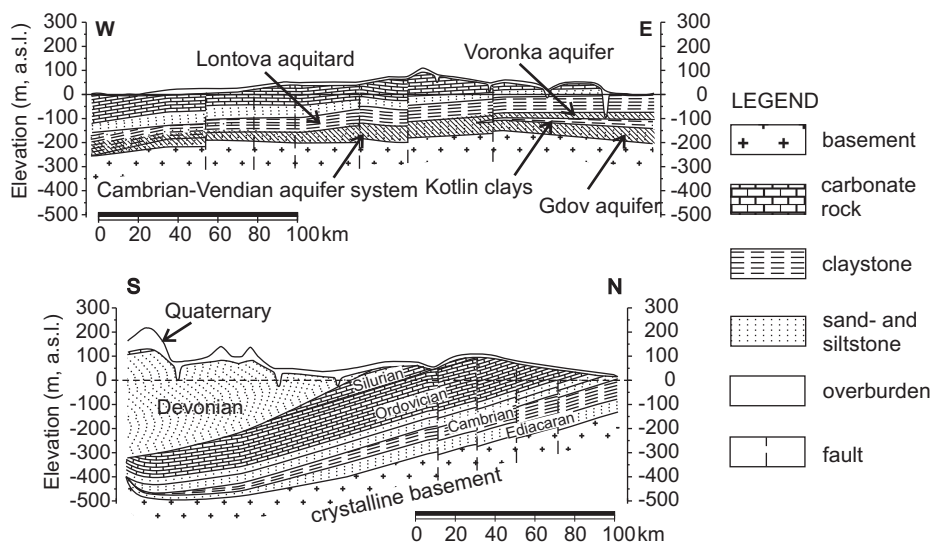
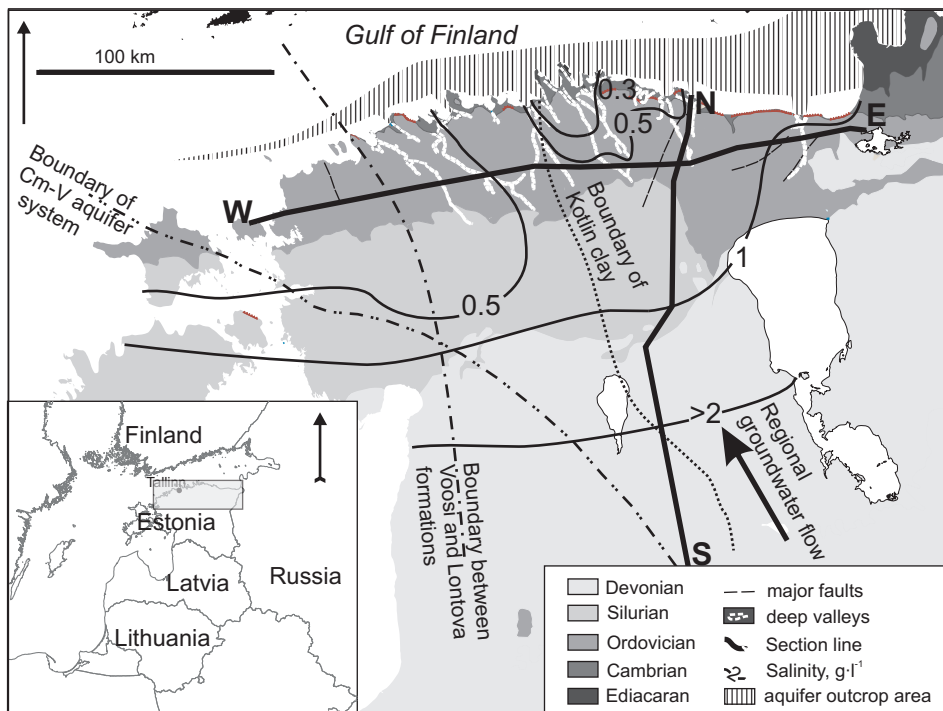


Figure 1. A geological scheme of Estonia and the West–East and the North–South cross-sections.

In the northeastern sector of the aquifer, the water bearing succession is divided by Kotlin clays (thickness up to 53 m) into two independent aquifers: the Upper Voronka (V_{2vr}) and the Lower Gdov aquifer (V_{2gd}). The Voronka aquifer consists of quartzose sand- and siltstone with a thickness of up to 45 m in northeastern Estonia. The Gdov aquifer is formed of up to 68 m thick mixed-grain sand- and siltstone and overlies directly the Precambrian basement. The clay of the Kotlin Formation serves as an upper confining unit. In northern Estonia, the conductivity of the water-bearing rock is $0.5\text{--}9.2\text{ m}\cdot\text{d}^{-1}$, with the average of $5\text{--}6\text{ m}\cdot\text{d}^{-1}$. Transmissivity in northeastern Estonia is $300\text{--}350\text{ m}^2\cdot\text{d}^{-1}$, decreasing in southerly and westerly directions (Karise 1997).

The chemical composition of the Cambrian–Vendian aquifer system varies both laterally as well as with depth. Generally, most of the water samples in the deeper part of the basin are of the Cl–Na, Cl–Na–Ca and Cl–Ca–Na type with TDS contents ranging from $1\text{--}22\text{ g}\cdot\text{l}^{-1}$. The shallow diluted water along the northern margin of the basin, in northern Estonia, is characterized by Cl–HCO₃–Na–Ca and Cl–HCO₃–Ca–Na type of waters with TDS content between $0.4\text{--}1.0\text{ g}\cdot\text{l}^{-1}$ (Savitskaja and Viigand 1994). In southern and central Estonia the aquifer system contains relict saline groundwater with TDS values of up to $22\text{ g}\cdot\text{l}^{-1}$. In this zone Cl[–] and Na⁺ predominate over all other ions (Karise 1997).

4. MATERIAL AND METHODS

In 1996–2009 the groundwater was sampled and analysed in operational private and/or municipal water supply and observation wells. The dataset was complemented with a selection of data collected from Cambrian–Vendian aquifer wells and published by Sokolov (1966), Kondratas (1967), Tratsevski (1967), Sapozhnikova (1967), Savitski et al. (1993), Savitskaja and Viigand (1994), Perens and Vallner (1997), Karro et al. (2004), Marandi (2007) and Vaikmäe et al. (2001; 2008). The quality of the published water analyses was screened and the samples in which the charge balance had exceeded $\pm 5\%$ were rejected. Altogether, the samples represent 150 wells all over Estonia. Radiocarbon has been analysed in 21 wells.

Sampling was done using production pumps in water supply wells and submersible pumps in observation wells. In the field, Eh, pH, electrical conductivity and temperature parameters were measured. The major anion and cation composition was analysed at Geochemistry Laboratory of Estonian Geological Survey.

Mineral, chemical, and grain size composition of Cambrian, Ediacaran, and Lower Ordovician deposits was investigated in 153 samples collected from 13 drillcores representing different lithofacies of the northern periphery of the basin. The mineralogical composition of sediments was determined by means of X-ray powder diffractometry in whole rock and in the clay ($<1 \mu\text{m}$) fraction in Institute of Geology, University of Tartu. Selected samples were observed under a scanning electron microscope using Zeiss 940D SEM in Institute of Geology, University of Tartu. The trace and major elements of 151 rock samples were determined by X-ray fluorescence spectroscopy in All-Russian Geological Institute, St.-Petersburg, Russia following standard procedures. The rock powders were analysed in Li-tetraborate homogenized pellets. The grain size of selected sandstone and claystone lithologies was determined by using standard sedimentation and sieve analysis, and petrophysical properties (effective porosity, wet, dry and grain densities) were measured on samples cut as cubes 24 mm in the Petrophysical Laboratory of Research Institute of Earth Crust of St. Petersburg University.

The hydrogeochemical parameters (ionic strength, activities, saturation indices and equilibrium diagrams) of water and brine samples were calculated by using the Geochemist Workbench 6.0® code.

Mixing calculation was performed assuming the three-component end-member (T) mixing model, with glacial melt-water (GM), basin formation (BF) and recent precipitation water (RP) component fractions. The mass balance of all fractions was assumed in Eq. (4.1):

$$\text{GM} + \text{BF} + \text{RP} = \text{T} \quad (6)$$

For a three-component model two conservative tracers were selected from dataset analysis, and a set of mass balance equations was solved by trial and error to satisfy the T=1 condition.

$$C_{GM}^{ta} Q_{GM} + C_{BF}^{ta} Q_{BF} + C_{RP}^{ta} Q_{RP} = C_T^{ta} Q_T \quad (7)$$

$$C_{GM}^{tb} Q_{GM} + C_{BF}^{tb} Q_{BF} + C_{RP}^{tb} Q_{RP} = C_T^{tb} Q_T \quad (8)$$

$$Q_{GM} = \frac{(C_T^{ta} - C_{RP}^{ta})(C_{BF}^{tb} - C_{RP}^{tb}) - (C_{BF}^{ta} - C_{RP}^{ta})(C_T^{tb} - C_{RP}^{tb})}{(C_{GM}^{ta} - C_{RP}^{ta})(C_{BF}^{tb} - C_{RP}^{tb}) - (C_{BF}^{ta} - C_{RP}^{ta})(C_{GM}^{tb} - C_{RP}^{tb})} Q_T \quad (9)$$

$$Q_{BF} = \frac{C_T^{ta} - C_{RP}^{ta}}{C_{BF}^{ta} - C_{RP}^{ta}} Q_T - \frac{C_{GM}^{ta} - C_{RP}^{ta}}{C_{BF}^{ta} - C_{RP}^{ta}} Q_{GM} \quad (10)$$

$$Q_{RP} = Q_T - Q_{GM} - Q_{BF}, \quad (11)$$

where C is the concentration of a tracer (a and b, respectively Cl^- in $mg \cdot l^{-1}$ and $\delta^{18}O$ in ‰ VSMOW) and Q is a mass-fraction of the given type of water.

Measurements of radiocarbon and stable isotopes of $\delta^{18}O$ and $\delta^{13}C$ in the water samples were performed at the Department of Isotope-Paleoclimatology of the Institute of Geology at Tallinn University of Technology. Radiocarbon activities in the groundwater were measured with a two-canal β -spectrometer. Stable isotope composition of oxygen in the water and carbon in the dissolved inorganic carbon were analysed on a Finnigan MAT Delta-E mass spectrometer. Analytical precision (2s) was 0.1‰. Results are expressed in per mil relative to Vienna Standard Mean Ocean Water (VSMOW) and Pedee Belemnite Standard (PDB) for oxygen and carbon, respectively. The dissolved inorganic carbon (DIC) was precipitated with either $Ba(OH)_2$ or $BaCl_2$.

SO_4^{2-} isotopes of a few selected wells were analysed at the Department of Isotope Hydrology of UFZ in Halle/Saale, Germany. For sulphur and oxygen isotope analyses, dissolved sulphate was precipitated as $BaSO_4$. Sulphur isotopic compositions were measured after conversion of $BaSO_4$ to SO_2 using an elemental analyser (continuous flow flash combustion technique) coupled with an isotope ratio mass spectrometer (ThermoFinnigan, Delta-S). Sulphur isotope measurements were performed with an analytical error of the measurement of better than ± 0.3 ‰, and the results are reported in delta notation ($\delta^{34}S$) as part per thousand (‰) deviation relative to the Cañon Diablo Troilite (CDT) standard. Oxygen isotope analysis on barium sulphate samples was carried out by high temperature pyrolysis at $1450^\circ C$ in a TC/EA connected to a Delta plus XL mass spectrometer (ThermoFinnigan) with an analytical precision of better than ± 0.5 ‰. Results of oxygen isotope measurements are expressed in delta notation ($\delta^{18}O$) as part per thousand (‰) deviation relative to Vienna Standard Mean Ocean Water (VSMOW).

For stable isotope measurements of carbonate cements a Micromass Isoprime multiflow system applying phosphoric acid dissolution method was used at the Institute of Geology, University of Copenhagen. The measured sample gas was compared with the isotope ratio of a standard gas derived from the reference standard LEO (with isotopic composition of 1.96 ‰ $\delta^{13}\text{C}$, -1.93 ‰ $\delta^{18}\text{O}$). The long-term reproducibility of the LEO standard is ≤ 0.10 ‰ for $\delta^{13}\text{C}$ and ≤ 0.20 ‰ for $\delta^{18}\text{O}$. Carbon isotope ratios were calibrated with respect to the Vienna Pee Dee Belemnite (VPDB) standard.

In the mass balance model of the carbon system in the Cambrian-Vendian aquifer the dissolution of carbonate minerals (calcite and dolomite) using Ca^{2+} and Mg^{2+} content as a proxy for old inorganic bicarbonate was assumed according to equations 1 and 2. For finding the amount of carbon originating from organic material in the total DIC pool, the equation proposed by van Stempvoort (2005) was used:

$$c(t) \cdot \delta^{13}\text{C}_{\text{DIC}(t)} = c(a) \cdot \delta^{13}\text{C}_{\text{DIC}(a)} + c(m) \cdot \delta^{13}\text{C}_{\text{DIC}(m)}, \quad (12)$$

where c is the concentration of DIC ($\text{mg}\cdot\text{l}^{-1}$), and indices t , a , and m refer to the total DIC in the methane-impacted groundwater, ambient DIC in the surrounding groundwater, and DIC produced by mineralization of organic carbon to DIC, respectively. The initial DIC was taken equal to the value of the calculated inorganic carbon concentration. The -10‰ was the chosen value for the background of $\delta^{13}\text{C}_{\text{DIC}}$, which corresponds to the conditions on the West-Estonian coast, where the lowest methane values in the Cambrian-Vendian aquifer occur.

The dissolution factors q_{dol} for estimating the effect of dolomite dissolution and q_{org} for estimating the effect of organic material degradation on radiocarbon activity were calculated with models proposed by Fritz and Clark (1997) and Pearson and Hanshaw (1970), respectively.

5. RESULTS AND DISCUSSION

5.1. Aquifer matrix

The whole-rock composition of the Cambrian-Ediacaran deposit in the basin shows distinct age and lithology controls (Raidla et al. 2006 – PAPER IV). The greenish-gray claystones of the Lontova and Lükati formations are composed of illite, illite-smectite, and in smaller quantities also chlorite and kaolinite; clay minerals compose 45–70% of the rock. The amount of clay minerals decreases to <20% in the Tiskre Formation and in the western facies (Voosi Formation), though locally it increases up to 35–50% in clay rich interlayers within silt- and sandstone dominated facieses. The illite and illite-smectite are the most abundant clay minerals, although in sandstones, where the clay mineral content is less than 10%, kaolinite may dominate over illite and illite-smectite (e.g. Paala Formation). Sandstones of Cambrian and the lowermost Ordovician are dominantly quartz arenites and subarkoses. The quartz content in Tiskre and Paala sandstones exceeds 90%, and averages 47% in all the studied samples (including claystone lithologies). The feldspars are almost exclusively K-feldspars (1–34%, in average 12%), with subordinate (<5%, usually close to 1%) amounts of albite. Content of mainly authigenic apatite (shell detritus of phosphatic brachiopods) and pyrite and/or hematite is in average close to 1% or less. No lithic fragments have been found in the sediment.

The authigenic carbonate minerals are represented mostly by Fe-rich dolomite, which is found in most samples (Figure 2). Its content is in the range of 0–29% with an average of about 3%. Also, calcite and siderite cements are occasionally reported (up to 19% and 8% of rock, respectively). Calcite is more abundant than siderite, its content only occasionally exceeds 1%. Petrographic observations indicate mainly poikilotopic type of the patchily or uniformly distributed cements. Paragenetic relationships suggest dolomite formation at latest phases of diagenesis, although in some cases simultaneous precipitation with authigenic clay minerals cannot be excluded (Raidla et al., 2006 – PAPER IV).

The whole rock composition of Ediacaran deposits is similar to their Cambrian lithological equivalents. The sandstone-dominated Gdov and particularly Voronka formations are rich in quartz (>30%) and feldspar (in average 4–10%). The composition of clay minerals of the Kotlin Formation is dominated by illite and illite-smectite, whereas clay minerals of Gdov and Voronka formations are considerably richer in kaolinite.

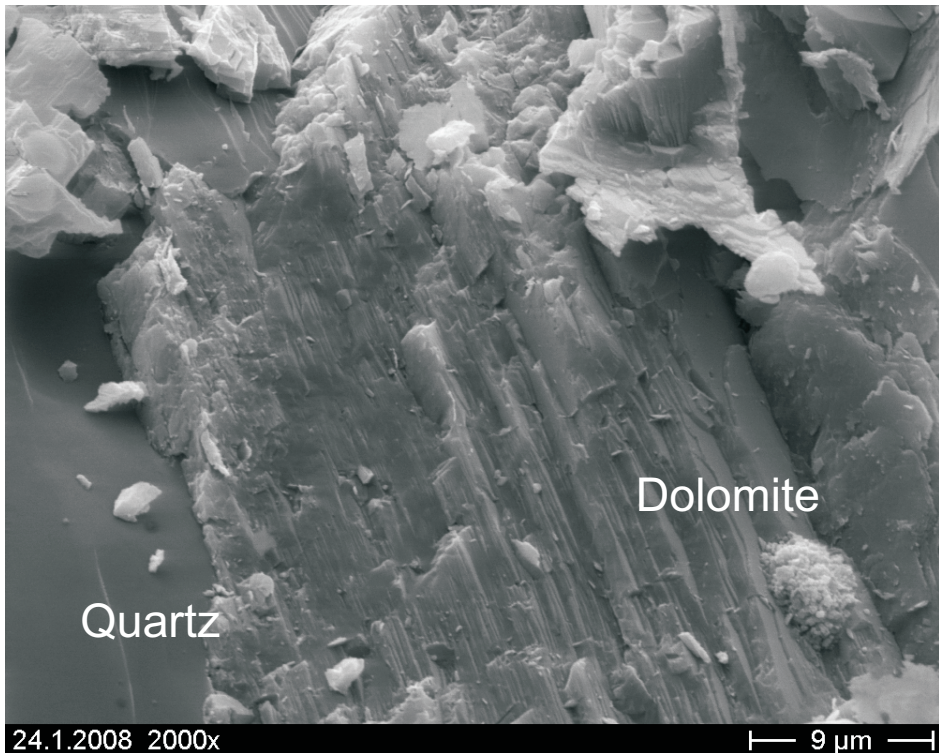


Figure 2. The secondary electron microscope image of carbonate cement in Cambrian sediments.

The sediments of the Cambrian-Vendian aquifer matrix are very loosely cemented and only scarce secondary carbonate cementation with rare occurrences of quartz cementation (Raidla et al. 2006 – PAPER IV) occurs. Carbonate cementation is the most abundant in the fine-grained sandstone and siltstone lithologies, being spatially related to lithological contacts with mud(clay)-stones. The highest dolomite content (10–20%) is identified in silty sandstones at contacts with clays of the Lontova Formation and the Ediacaran Kotlin clays. Carbonate cementation of siliciclastic rocks may commence at very early stages of diagenesis influenced by marine or mixed marine-meteoric waters, or anoxic pore-waters in which the dissolved sulphate ions have been removed by bacterial reduction (Baker and Kastner 1981). The marine water environment, related to compaction fluid flow, was established for carbonate cement precipitation from stable carbon isotope studies in the southern periphery of the basin Baltic Basin (Schleicher 1994). At later stages of the diagenesis the carbonate precipitation could have occurred in pore-waters where pH was buffered by aluminosilicate equilibrium or by organic acids, and the excess CO₂ derived from thermal oxidation of organic matter was eliminated by simultaneous carbonate precipitation (Smith and Ehrenberg 1989). However, the Cambrian clays in

northern part of the basin contain 0.79% to 2.56% of dispersed diagenetically immature organic material (Talyzina 1998). The $\delta^{13}\text{C}$ -values of the organic matter are about -31% VPDB (Bityukova et al. 2000), which is quite characteristic for organic matter of the Cambrian origin (Schidlowski 1988), and typical for dispersed organic matter of sapropelitic type of Cambrian sedimentary rocks (Sidorenko and Sidorenko 1975). This would suggest that dolomite cementation in the aquifer matrix resulted from ions released during the illitization (e.g. Wintsch and Kvale 1994). This could have enhanced the secondary dolomite precipitation preferentially close to the claystone-silt/sandstone interfaces where dolomite cementation in Cambrian-Ediacaran rocks is mostly found (Raidla et al. 2006 – PAPER IV). The $\delta^{13}\text{C}$ analysis of these carbonate cements in the central part of the research area shows a negative composition varying from -10.7 to -18.7% VPDB, which suggests that some of the organically derived carbon was used during dolomite precipitation.

The crystalline basement in northern Estonia is composed mostly of mafic regionally metamorphosed rocks of Paleoproterozoic age (1.9–1.8 Gyr). The rock types in western part of the area are characterized by migmatized pyroxene – amphibole gneisses. The rocks in the eastern part are predominantly high-alumina gneisses. The Paleoproterozoic rocks are intruded by several rapakivi granite plutons of 1.63 Gyr age (Kirs et al., 2009)

5.2. Groundwater mixing and dilution

Chemical composition of the Cambrian–Vendian aquifer varies both laterally and vertically. Generally, most of the water samples in the deeper part of the Baltic basin belong to the Cl–Na, Cl–Na–Ca and Cl–Ca–Na type with TDS contents ranging from $1\text{--}22\text{ g}\cdot\text{l}^{-1}$ (Karise 1997). The shallow diluted water along the northern margin of Estonian territory is characterized by Cl–HCO₃–Na–Ca and Cl–HCO₃–Ca–Na type of waters with TDS content between 0.4 and $1.0\text{ g}\cdot\text{l}^{-1}$ (Vaikmäe et al. 2008 – PAPER III). Changes in Na⁺ and Cl[−] compositions on the northern margin of the aquifer system are significantly larger in horizontal than in vertical direction. Typically, Na⁺ and Cl[−] concentrations increase eastward. The content of Na⁺ and Cl[−] varies from 20 to $600\text{ mg}\cdot\text{l}^{-1}$ and from 40 to $1050\text{ mg}\cdot\text{l}^{-1}$, respectively, exhibiting the highest values in the eastern part of the country (Raidla et al. 2009 – PAPER I).

Mokrik (1997) suggests that meteoric waters replaced the synsedimentary marine fluids within the aquifer strata during the Middle-Late Cambrian uplift of the area, while marine fluids recharged the aquifer during Ordovician–Devonian when the basin was considerably subsided. The Ediacaran–Cambrian, or the overlying Ordovician and Silurian sediments do not contain any known bedded evaporites and the source for elevated salinity is also unknown. Brines of the Baltic Basin are typical deep sedimentary basinal Ca–Na–Cl fluids enriched with respect

to Ca^{2+} and depleted in Mg^{2+} and SO_4^{2-} , compared with the evapo-/cryo-concentration trend of the modern seawater (e.g. Lowenstein et al. 2003).

The salinity of the groundwater shows rather uniform increase with the increasing depth of the aquifer. However, in dilute shallow groundwater the salinity increase with depth is much slower compared to deeply buried waters, and the concentration of the predominant anion, Cl^- , is on average less than $1,000 \text{ mg}\cdot\text{l}^{-1}$ at 400–500 m depths, whereas from depths of about 500 m the Cl^- content increases rapidly to more than $165,000 \text{ mg}\cdot\text{l}^{-1}$ at a depth of about 2,000 m (Sokolov 1966). The Na^+ , K^+ and Cl^- concentrations plot along the seawater dilution/evaporation line, indicating the simple dilution-concentration mechanism of the two major end-member sources. However, the $\text{Na}^+ + \text{K}^+ / \text{Cl}^-$ ratios of the most dilute fresh waters deviate from the main dilution-concentration trend, which indicates three-component mixing (Figure 3, Raidla et al. 2009 – Paper I).

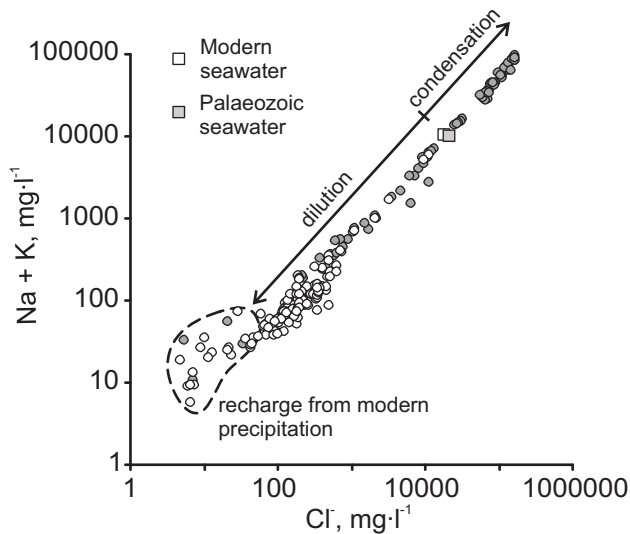


Figure 3. $\text{K}^+ - \text{Na}^+$ and Cl^- relations in Cambrian-Vendian aquifer groundwaters. The diluted waters that deviate from trend are of $\text{Cl}^- - \text{HCO}_3^- - \text{Na} - \text{Ca}$ type water influenced by modern meteoric recharge.

The understanding of three-component origin is also supported by the oxygen isotope systematics of groundwaters suggesting mixing of basinal brine and diluted (meteoric) water carrying of two different isotopic signatures corresponding to glacial meltwater and modern precipitation. Most of the groundwaters in North-Estonian part of the Cambrian-Vendian aquifer have a strongly depleted $\delta^{18}\text{O}$ composition of less than -18‰ compared with that of modern precipitation, or possible paleoseawater of -11‰ and 0 to -2‰ , respectively (Muehlenbachs 1998; IAEA/WMO 2008).

The results of mixing calculations (Raidla et al. 2009 – PAPER I) suggest that in the most depleted shallow waters at the northern margin of the basin the glacial component comprises more than 80% of the water. The content of glacial component decreases and, accordingly, the brine component increases gradually with the depth, and at ~700 m the glacial component has decreased to about 30–40%.

More positive $\delta^{18}\text{O}$ values in the eastern part of the research area do not necessarily reflect the result of mixing between glacial water and brine. Despite the changes in Cl^- concentration, $\delta^{18}\text{O}$ values remain the same (Figure 4). Moreover, the mixing model suggests recent and glacial water ratio of 40% and 60%, respectively (Raidla et al. 2009 – PAPER I), but lower ^{14}C concentrations in North-East Estonia (Raidla et al. – PAPER II) suggest long residence time without significant intrusion of modern waters. This phenomenon could be the result of, first, isotopic difference between ice compositions of the glacial tongues. Second, excess chlorine could have originated from dissolution of evaporites, and not from mixing with brine. Although the Ediacaran or Cambrian sediments contain no known bedded evaporites (Raidla et al. 2006 – PAPER IV), then $\delta^{34}\text{S}_{\text{SO}_4}$ composition of dissolved sulphate in North-East Estonian part of the aquifer points to high content of evaporitic sulphate (Raidla et al. – PAPER II).

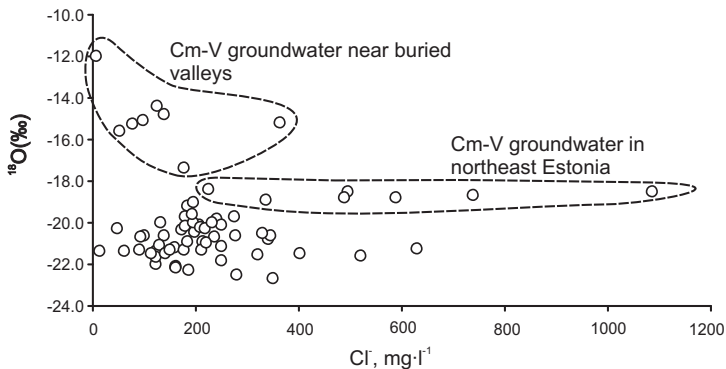


Figure 4. $\delta^{18}\text{O}$ and Cl^- relations in the Cambrian-Vendian aquifer system groundwaters.

The influx of modern meteoric water is recognized in rather large isolated areas along the northern margin of North-Estonia, where deep pre-Quaternary valleys cut the aquitard above the aquifer. The deeper parts of the Cambrian-Vendian aquifer system in eastern Estonia are efficiently isolated by the Kotlin aquitard, but the influx of modern meteoric water occurs in the coastal zone of the Voronka subaquifer (Figure 5). At these places the groundwater composition is characterized by the diluted $\text{HCO}_3\text{-Cl-Ca-Na}$ or $\text{HCO}_3\text{-Cl-Na-Ca}$ type groundwaters with TDS of 170–600 $\text{mg}\cdot\text{l}^{-1}$. The diluted waters containing over 90% of modern meteoric water have replaced the mixed glacial-brine fluids (Raidla et al. 2009 – PAPER I).

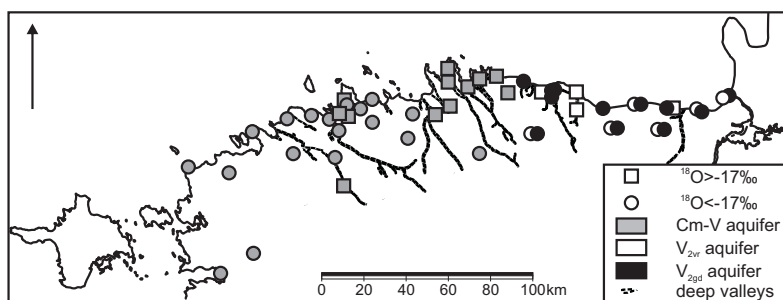


Figure 5. Distribution of diluted $\text{HCO}_3\text{-Cl-Ca-Na}$ or $\text{HCO}_3\text{-Cl-Na-Ca}$ type groundwaters ($\delta^{18}\text{O} > -17\text{‰}$) and glacial origin groundwater ($\delta^{18}\text{O} < -17\text{‰}$) in the Cambrian-Vendian aquifer system.

5.3. Carbon and sulphate system of groundwater

Concentration of HCO_3^- , the main carbon carrier in the aquifer, increases gradually eastwards from about $100 \text{ mg}\cdot\text{l}^{-1}$ in West-Estonia to $250 \text{ mg}\cdot\text{l}^{-1}$ in North-East Estonia. In East-Estonia, where the aquifer system is divided into the upper Voronka and the lower Gdov subaquifers, the HCO_3^- concentration in the former is $150\text{--}250 \text{ mg}\cdot\text{l}^{-1}$, and in the latter, mostly $120\text{--}170 \text{ mg}\cdot\text{l}^{-1}$. The amounts of CO_3^{2-} and free CO_2 in DIC are insignificant (Raidla et al. – PAPER II), and the HCO_3^- can be considered representing the $\text{DIC}_{\text{total}}$.

The $\delta^{13}\text{C}_{\text{DIC}}$ of the water in the Cambrian-Vendian aquifer shows considerably depleted composition of carbon in the range of -11 and -24 ‰ (exceptionally -34 ‰) VPDB. The isotope composition of carbon is more positive in wells of the western part of the study area compared to those in the east. The most positive $\delta^{13}\text{C}_{\text{DIC}}$ values are found in West-Estonian coastal areas (-11‰ to -12‰ VPDB). In the central part of the studied area the $\delta^{13}\text{C}_{\text{DIC}}$ values are about -16‰ to -18‰ VPDB, while in the eastern part the $\delta^{13}\text{C}_{\text{DIC}}$ values of Voronka and Gdov subaquifers are distinctly different. $\delta^{13}\text{C}_{\text{DIC}}$ values of the Voronka aquifer are relatively stable at about -17‰ , whereas the wells of the lower Gdov aquifer show $\delta^{13}\text{C}_{\text{DIC}}$ value variation from -17‰ to -24‰ (Raidla et al. – PAPER II).

At the same time the $\delta^{13}\text{C}$ in the uppermost groundwater in an active exchange zone recharged by modern precipitation is characterized by rather uniform values of -10‰ VPDB (Vaikmäe et al. 2001). The latter are controlled by the equilibrium between CO_2 derived from plant respiration and degradation of organic material in the soil ($\delta^{13}\text{C}$ in the range of -20 and -24‰ , Salamons and Mook 1986), and by dissolution of carbonate minerals in the overlying marine Palaeozoic carbonate rocks and Quaternary sediments ($\delta^{13}\text{C}$ values around 0‰ , Kaljo et al. 2004).

Usually, $\delta^{13}\text{C}_{\text{DIC}}$ values in the water increase concurrently with the increase in DIC through dissolution of carbonate (e.g. Clark and Fritz 1997). Raidla et

al. – PAPER II shows an opposite trend in the Cambrian-Vendian groundwater in northern Estonia. Similar depletion in $\delta^{13}\text{C}_{\text{DIC}}$ values while DIC increases have been noticed in the groundwaters affected by input of some organic carbon (van Stempvoort et al. 2005, McIntosh and Walter 2006, Herczeg et al. 1991). Nevertheless, typical behavior of DIC and $\delta^{13}\text{C}$ ratios can be seen in the wells situated next to deep buried valleys, which are recharged by modern precipitation waters.

There is also a negative co-variance between HCO_3^- and SO_4^{2-} , where higher HCO_3^- concentrations correspond to lower SO_4^{2-} concentrations. Moreover, the most negative $\delta^{13}\text{C}_{\text{DIC}}$ values are found in waters with the lowest SO_4^{2-} concentrations (Raidla et al. – PAPER II). This indicates anaerobic methane oxidation that uses SO_4^{2-} as the terminal electron acceptor, whereas reduction of SO_4^{2-} is typically catalyzed by bacteria of the genus *Desulfofibrion* (e.g. Jørgensen 1982) producing dissolved sulphide and mineralized carbon. Direct sources of SO_4^{2-} , such as gypsum deposits, occur in neither Cambrian nor Ediacaran rocks (Raidla et al. 2006 – PAPER IV), and most of the sulphate is probably derived from oxidation of sulphide minerals (mainly pyrite), which are common in both Ediacaran and Cambrian rocks (Raidla et al. 2006 – PAPER IV). The idea of bacterial sulphate reduction is supported by correlation between $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ in the groundwater of the Cambrian-Vendian aquifer, which has been interpreted as evidence of bacterial activity (e.g. van Stempvoort et al. 2005)

Microbial influence is also supported by an occurrence of methane, which is common in Cambrian-Vendian groundwater (up to 30% of the dissolved gases, Pihlak et al. 2003). The $\delta^{13}\text{C}_{\text{CH}_4}$ composition of the Cambrian-Vendian groundwater varies typically from -74.6‰ to -92‰ VPDB (Vaikmäe et al. 2001, Voitov et al. 1982), which suggests a bio-organic origin of the methane (Clark and Fritz 1997). The source of methane found in the sediments of the Cambrian-Vendian aquifer system is unknown. It is generally assumed that the methane originates from anaerobic decomposition of sediments of the Emian interglacial age ($\sim 110,000$ BP) and from organic sediments older than 30,000 BP rich in organic matter (peat) that occur in the Gulf of Finland along the northern coast of Estonia (Raukas and Kajak 1997). It is possible that the meltwater, which penetrated into the Cambrian and Ediacaran rocks through outcrop areas in the Baltic Sea and the Gulf of Finland, was enriched with this methane. Later, CO_2 and methane from decomposition of organic matter in Cambrian and Ediacaran clays could have been added. The co-existence of SO_4^{2-} and methane could have influenced the carbon system of the aquifer's water by adding negative carbon to the groundwater DIC during methane reduction by *Desulfovibrio desulfuricans*, who used SO_4^{2-} as an oxidant.

The Ca^{2+} and Mg^{2+} activity ratio in Cambrian-Vendian groundwaters suggests equilibrium with sedimentary dolomite and calcite (Raidla et al. 2009 – PAPER I), which implies that the dissolution and isotope exchange with carbonate minerals has also influenced the isotopic composition of the Cambrian-Vendian groundwater. Siliciclastic rocks of the Cambrian-Vendian aquifer

contain carbonate cement, mainly Fe-rich dolomite (Raidla et al. 2006 – PAPER IV). The cemented zones are in most cases found at contacts with large green-clay beds of the Cambrian sediments and the Ediacaran Kotlin clays. The $\delta^{13}\text{C}$ analysis of these carbonate cements shows a remarkably negative composition, which varies from -10.3 to -18.8% VPDB in the central part of the study area.

$\delta^{34}\text{S}$ composition in Voronka and Gdov aquifers seems to have undergone similar sulphate reduction process, and yet there is a considerable difference in HCO_3^- content and $\delta^{13}\text{C}_{\text{DIC}}$ values (Raidla et al. – PAPER II). The differences are probably caused by the uneven distribution of dolomite cement and organic material in the rocks of both aquifers. In the Voronka aquifer, which lies between clay layers, the dolomite cements are more widely distributed than in the lower Gdov layer (Raidla et al. 2006 – PAPER IV). Therefore, the amount of bicarbonate, which was added by the meltwater infiltrating into the aquifer as a result of cement dissolution, is bigger. Even though the $\delta^{13}\text{C}$ of dolomite cement is remarkably negative, it is still much more positive than the value of $\delta^{13}\text{C}_{\text{DIC}}$ added through bacterial reduction. Cement dissolution has most likely levelled $\delta^{13}\text{C}$ values, which is why $\delta^{13}\text{C}_{\text{DIC}}$ in the wells of the Voronka subaquifer is more uniform than in those of the Gdov subaquifer. Also, in the Voronka subaquifer, which is confined between massive clay beds, carbon from decomposition of old Cambrian and Ediacaran organic material with $\delta^{13}\text{C}_{\text{org}}$ values of -30% could predominate. In contrast, the most negative $\delta^{13}\text{C}_{\text{DIC}}$ values (-17 to -34%) found in the Gdov subaquifer suggest that the bicarbonate probably derived mainly from oxidation of methane that migrated from pre-glacial Late-Weichselian organic rich sediments in the Gulf of Finland distributed along the northern coast of Estonia. The decreasing trend of $\delta^{13}\text{C}_{\text{DIC}}$ values towards the coastal area (Figure 6) supports this hypothesis.

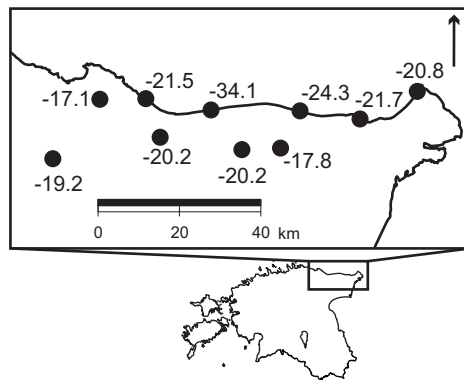


Figure 6. $\delta^{13}\text{C}_{\text{DIC}}$ (‰) values in Gdov subaquifer groundwater at the North-East Estonia.

5.4. ¹⁴C age and evolution of groundwater in the Cambrian –Vendian aquifer system

Based on the mass balance equation, it can be stated that the main processes, which have diluted the ¹⁴C concentration besides radioactive decay are dissolution of carbonate minerals, methane reduction by bacteria, and decomposition of geologically old immature organic materials (Raidla et al. – PAPER II). The results of mass balance model calculations show that the best fit for carbonate input was achieved by assuming dissolution of carbonates (dolomite and calcite) in a closed system, i.e. under conditions of a limited inflow of CO₂.

In radiocarbon dating, other geochemical processes besides the above-described dissolution of carbonate cements and the effect of organic carbon must also be considered. In Paper II we show that cation exchange has influenced the Ca²⁺ and Mg²⁺ contents in the entire Voronka subaquifer, and in some parts of the Gdov subaquifer. In order to overcome similar problems, Herczeg (1991) has used Cl⁻ as a geochemically conservative tracer for standardizing Mg²⁺ and Ca²⁺ according to Cl⁻/Na⁺ ratio. In addition, Ca²⁺ in the central part of the research area has been influenced by Ca²⁺ originating from the bedrock. Since in the central part of the research area calcite cement is lacking and carbonates are represented only by dolomite, Mg²⁺ could be used as a proxy for Ca²⁺ for estimating carbonate dissolution. This method, however, is not as reliable, because in Fe-rich dolomite, as is characteristic to Cambrian and Ediacaran sediments (Raidla et al. 2006), some of Mg²⁺ has been replaced by iron. Still, quite good modelling results (relation between measured and calculated concentrations of HCO₃⁻ are 0.8 to 1.2) in the central part of the study area (Raidla et al. – PAPER II) suggest that this approach does not cause considerable shifts in calculating radiocarbon's residence time in the Cambrian-Vendian aquifer.

The carbon originating from dissolution of carbonate minerals was accounted using equations modified after Fritz and Clarke (1997):

$$q_{\text{dol}} = \frac{m\text{HCO}_3^-}{m\text{HCO}_3^- + 2m\text{Mg}^{2+}} \quad (13),$$

$$q_{\text{dol}} = \frac{m\text{HCO}_3^-}{m\text{HCO}_3^- + 2m\text{Ca}^{2+}} \quad (14),$$

$$q_{\text{cal}} = \frac{m\text{HCO}_3^-}{m\text{HCO}_3^- + (m\text{Ca}^{2+} - m\text{Mg}^{2+})} \quad (15).$$

A correction factor to estimate the effect of organic material (q_{org}) on the true radiocarbon age was found according to Pearson and Hanshaw (1970):

$$q_{org} = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{org}}{\delta^{13}C_{init} - \delta^{13}C_{org}} \quad (16)$$

where,

$\delta^{13}C_{DIC}$ – $\delta^{13}C$ of groundwater carbonates

$\delta^{13}C_{org}$ – $\delta^{13}C$ of carbon originating from an organic source

$\delta^{13}C_{init}$ – $\delta^{13}C_{DIC}$ of groundwater carbonates before their encounter with the carbon originating from an organic source (≈ -10 ‰).

The values of q_{dol} decrease slightly towards the east. The highest values of q_{org} are represented in the western part of the research area and in the Gdov subaquifer in the eastern part of the research area (PAPER II – Raidla et al.). These results are in agreement with weak influence of organic carbon in western part of the aquifer system.

The corrected radiocarbon (residence) age of the water was found using equation 17:

$$T = \frac{5730}{\ln 2} \cdot \ln \frac{q_{dol} \cdot q_{cal} \cdot q_{org} \cdot A_0}{A_{measured}} \quad (17)$$

where:

T – time

A_0 – modern ^{14}C activity

$A_{measured}$ – measured ^{14}C activity

q_{org} – correction values of organic carbon

q_{cal} – correction values of calcite

q_{dol} – correction values of dolomite

After converting the measured radiocarbon activities of the groundwater into true residence time, the obtained age of the groundwater was between 12,000 – 25,000 radiocarbon years, which is approximately 10,000 years younger than the conventional radiocarbon age measurements have given previously (Raidla et al. – PAPER II). In this case the age of the groundwater in the Cambrian–Vendian aquifer is coeval with the advance and maximum extent of the Weichelian Glacier that covered Estonian territory ~27,000 to 11,000 radiocarbon years ago (Raukas and Kajak 1997, Kalm 2005).

Based on chemical composition of groundwater, and on the geological setting of the area, the study region can be divided into western, eastern and central zones (Figure 7). The western zone can be defined westwards from the boundary of the

Lontova-Voosi Formation, where Lontova clays are graded into silt- and sandstones of the Voosi Formation, whereas the aquifer itself becomes considerably thinner (Figure 1). The results of radiocarbon age calculations and sulphate isotope's composition suggest that the groundwater's chemical, isotopic, and also dynamic evolution have been different in western Estonia compared to the rest of the study area (Raidla et al. – PAPER II). Higher SO_4^{2-} concentrations in the western zone compared with those in central and eastern areas of the aquifer result from lower content of organic material and methane and/or more intensive pyrite oxidation. It is possible that oxygenated glacial meltwater penetrated into the aquifer under hydrostatic pressure of the glacier more easily in the western zone of the aquifer. This hypothesis is supported by different enrichment of $\delta^{18}\text{O}_{\text{SO}_4}$, which could indicate that isotopically heavy atmospheric oxygen (+23.5‰, Kroopnik and Craig 1971) affected the sulphate's oxygen system in the western part of the research area. This understanding is also supported by $\delta^{18}\text{O}$ analyses from the groundwater of the Ordovician-Cambrian aquifer system above the Lontova-Lükati aquitard. While in central and eastern part of the Ordovician-Cambrian aquifer $\delta^{18}\text{O}$ analyses show more positive values than -16‰ (remaining mostly close to -14‰), in the western part of the study area much more negative values predominate (-18.5 to -19.5‰) (Savitskaja et al. 1995, Vaikmäe et al. 2001). However, it is unclear how this paleowater has preserved these negative values, as the Ordovician-Cambrian aquifer is relatively unprotected from the influence of modern meteoric water. Groundwater ^{14}C residence times are also the shortest in the western zone.

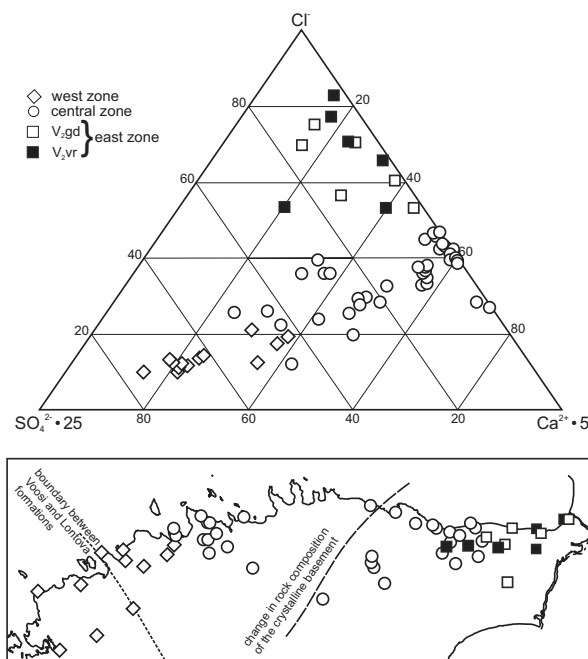


Figure 7. Ternary diagram of the studied groundwater and the distribution of three hydrogeochemical zones.

The central zone surrounds the active Cambrian-Vendian water exchange area in North-Estonia, where numerous buried valleys allow modern precipitation waters to infiltrate the Cambrian-Vendian aquifer. Ca^{2+} concentrations in the central zone increase gradually from west to east and decline abruptly in the eastern part. The increase coincides with the change in the rock composition of the crystalline basement (Raidla et al. – PAPER II). Crystalline rocks in the east are composed of metamorphosed alumo-gneisses with CaO content of 2–3%. In the west metamorphosed mafic rocks with CaO content of 6–7% occur. Also, the upper surface of the crystalline basement is strongly weathered and the thickness of the weathering crust increases from about 1 m to 150 m in the western and eastern part of Estonia, respectively (Puura et al. 1983). The distribution line of Ca^{2+} rich waters runs further east from where the change in the rock composition of the crystalline basement occurs. This indicates that these waters could have infiltrated in west-to-east/northwest-to-southeast direction.

The content of dissolved solids (TDS) is highest in the eastern zone of the research area, where Cl^- ion predominates. This zone is also characterised by increasingly more positive $\delta^{18}\text{O}_{\text{water}}$ values (–20 to –18.5‰). The eastern zone of the Cambrian-Vendian aquifer is characterized by a more restricted water exchange (lower permeability) than in other parts of the research area. This results from a greater thickness and a more clayey composition of the Lontova-Lükati aquitard, as well as from a smaller number of buried valleys that are mostly found in the western part of the study area. Geologically, the entire eastern zone is divided into two subaquifers, whereas the borderline between central and eastern zones of the Voronka subaquifer does not correspond to central and eastern zones of the Gdov subaquifer. This could be explained by impeded infiltration conditions in the Voronka aquifer.

Groundwater ^{14}C residence times increase in west-to-east direction. In the western zone groundwater residence times correspond to the glacier's late and early regression period, in the central zone mainly to the late regression period, and in the eastern zone only to the transgression period. It shows that glacial meltwater intrusion in central and eastern zones of the aquifer had occurred mostly during the glacier's advance into the area, whereas the western part of the aquifer has had active water exchange during the entire existence of the glacier. It could be explained by better isolation of the aquifer system in the eastern zone and reduced infiltration during the existence of the glacier.

6. CONCLUSIONS

1. The Ca^{2+} and Mg^{2+} activity ratio in Cambrian-Vendian groundwaters suggests equilibrium with sedimentary dolomite and calcite, which implies that the dissolution and isotope exchange with carbonate minerals has influenced the isotopic composition of the Cambrian-Vendian groundwater.
2. The $\delta^{13}\text{C}$ analysis of the carbonate cements from Cambrian and Ediacaran rocks shows a remarkably negative composition of $\delta^{13}\text{C}_{\text{carb}}$, which varies from -10.7 to -18.7 ‰ VPDB in the central part of the research area. Depleted $\delta^{13}\text{C}$ values suggest involvement of organic carbon, which was probably derived from organic material occurring in Cambrian and Ediacaran clays.
3. $\text{Na}^+ + \text{K}^+ / \text{Cl}^-$ ratio and salinity trends of Cambrian–Vendian groundwaters suggest mixing of different waters along the northern margin of the basin – (1) saline basinal brine and (2) diluted, meteoric water. The oxygen isotope systematics of these waters suggests that a three-component mixing occurs in so far as the diluted (meteoric) water carries two different isotopic signatures that correspond to glacial meltwater and modern precipitation.
4. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and Cl^- values in the eastern part of the research area do not necessarily reflect the result of mixing between glacial water and brine, but may show dissolution of evaporates and the isotopic difference between glacial meltwaters.
5. $\delta^{13}\text{C}_{\text{DIC}}$ values become constantly more negative from west to east, and are inversely proportional to HCO_3^- concentrations. $\delta^{13}\text{C}_{\text{DIC}}$ values are more positive in the Voronka subaquifer than in the lower Gdov subaquifer.
6. The isotope composition of sulphur suggests two sources: (1) likely a evaporitic sulphate in North-East Estonia, and (2) pyrite elsewhere in the study area. Sulphate isotope values suggest bacterial activity in groundwaters of the Cambrian-Vendian aquifer system. During the process the bacteria reduced methane by using SO_4^{2-} as the source for oxygen.
7. The most important processes influencing the true radiocarbon age are the dissolution of carbonate minerals and the impact of carbon supplied by bacterial activity.
8. Based on isotopic and chemical data from the groundwater of the Cambrian-Vendian aquifer, and the geological setting of the area, the study area can be divided into western, eastern and central zones.
9. The results of radiocarbon age calculations and sulphate isotope's composition suggest that the groundwater's chemical, isotopic, and also dynamic evolution have been different in western Estonia compared to the rest of the study area
10. The calculated groundwater residence time by ^{14}C method suggests age between 12,000 and 25,000 radiocarbon years, which corresponds to the existence of the Weichselian ice shield in Estonian territory. Important differences in residence times appear between samples from West-Estonia

and those from the rest of the research area, probably due to different infiltration mechanisms. It is possible that glacial meltwater in central and eastern zone of the aquifer occurred during the glacier's advance and early regression period into the area, whereas the western part of the aquifer has had active water exchange during the entire existence of the glacier.

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SUMMARY IN ESTONIAN

Eesti Kambrium-Vendi põhjaveeladestiku vete keemiline ja isotoopne areng

Käesolev doktoritöö uurib Kambrium-Vendi põhjaveeladestiku vete keemilise ja isotoopkoostise kujunemist.

Põhja-Eestis Kambrium-Vendi põhjaveeladestiku vetele on iseloomulikud madalad ^{14}C aktiivsused (1.4–6.8 pmc) ja võrreldes kohalike sademetega (–10 kuni –12‰VSMOW) märksa negatiivsemad $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ väärtused (–22 kuni –18‰VSMOW). Seda nähtust on seletatud Kambrium-Vendi põhjavete pärinemisega mandriliustiku sulavetest, mis kattis Eesti territooriumi 27000 kuni 10000 radiosüsiniku aastat tagasi.

^{14}C aktiivsused Kambrium-Vendi põhjavees annavad põhjavee atmosfäärist isoleerumise ajaks 35000 kuni 15000 radiosüsiniku aastat, mis ei sobi eelnimetatud hüpoteesiga. Samas on paljud autorid tõestanud, et läbi geokeemiliste protsesside muutuvad ^{14}C dateeringud põhjaveest näivalt vanemaks. Tegelikult ^{14}C vanuse arvutamiseks on vaja leida geokeemilised protsessid, mis on mõjutanud põhjavee keemilise ja isotoopkoostise kujunemist.

Kambrium-Vendi põhjaveeladestiku kivimites levib karbonaatne, peamiselt rauddolomiidiga esindatud tsement, mille isotoopkoostis ($\delta^{13}\text{C}$ –11 kuni –18‰) viitab orgaanilisele päritolule. Selle nähtuse tõenäoliseks põhjuseks on peetud peenhõljumina meremutta sadestunud orgaanilist ainet (väikesed mikroorganismid ning ka surnud orgaaniline materjal), mille hilisemal lagunemisel on tekkinud süsinikdioksiid, mis võibki olla Kambriumi ja Ediacara setetes leviva karbonaatse tsemendi lähtematerjal.

Kambrium-Vendi põhjaveeladestiku vete keemiline koostis on kujunenud pikaajalise vee ja ümbritsevate kivimite vastastikuse mõju toimetel. Leitud segunemismudel kinnitas mageda liustikulise ja relikitse mineraalvee segunemist. Kui Kambrium-Vendi põhjaveeladestiku põhjaosa vetest moodustab 80% liustikulise päritoluga vesi, siis põhjaveeladestiku lõunaosas (~700 m sügavusel) domineerib relikadne mineraalvesi ning liustikulise päritoluga põhjavee osakaal on seal langenud 30–40%. Uurimisala kirdeosas, kus segunemismudel annab tänapäevaste vete osakaaluks kuni 40%, on mõõdetud väga madalad ^{14}C aktiivsused, mis ei vasta niivõrd ulatuslikule tänapäevase vee sissetungile. On põhjust arvata, et sealne isotoop- ja keemiline koostis ei peegelda mitte segunemis- vaid lahustumisprotsesse.

Kambrium-Vendi põhjaveeladestiku süsinikuringet on oluliselt mõjutanud Kambriumi ja Ediacara savides leviv orgaaniline materjal, mille lagunemisel vabanenud süsinik on osalenud nii settimis- kui lahustumisprotsessides. Uurimisala idaosas, kus põhjaveekihistik jaguneb ülemiseks Voronka ja alumiseks Gdovi põhjaveelademeks, on märgata ilmseid erinevusi põhjavee süsinikuringes. Nimelt esinevad suuremad HCO_3^- kontsentratsioonid ja positiivsemad $\delta^{13}\text{C}_{\text{DIC}}$ väärtused enamasti Voronka põhjaveelademes. Selle põhjuseks on

orgaanilise materjali, metaani ja karbonaatse tsemendi parem esindatus Voronka põhjaveelademe kivimites.

Peamised orgaanilise materjali lagundajad põhjavees on bakterid, kes kasutavad redutseerijatena ära erinevaid hapnikukandjaid. Sulfaatioon SO_4^{2-} , mis on üsna tavaline põhjavees, on ka üks olulisemaid elektronaktseptoreid orgaanilise materjali bakteriaalsel lagundamisel. Sulfaatiooni isotoopkoostis Kambrium-Vendi põhjaveeladestiku vetes näitas selget rikastumistrendi, mille põhjuseks võib pidada bakteriaalset tegevust. Kõige väiksem sulfaatioonide rikastatus oli uurimisala lääneosas ning isotoopne rikastatus tõuseb ühtlaselt ida suunas.

Orgaanilisest materjalist pärinev süsinik on oluliselt mõjutanud näivat ^{14}C vanust nii otseselt läbi bakteriaalsete oksüdeerimisprotsesside kui ka kaudselt, dolomiitse tsemendi lahustamisega. Nende protsesside mõju ^{14}C vanusele on kõige väiksem uurimisala lääneosas ning suureneb ida suunas koos kambriumi kivimite paksuse ja savikuse kasvuga. Töö käigus selgus ka aluspõhja kivimite ja kationivahetusprotsesside oluline geokeemiline mõju ^{14}C vanuse arvutustele.

Esitatud süsiniku geokeemilise mudeli alusel tehtud ^{14}C vanuse parandusarvutused andsid Kambrium-Vendi põhjaveeladestiku vete vanuseks 12000 kuni 25000 radiosüsinikuaastat, mis vastab ajavahemikule, mil Eesti territoorium oli kaetud mandriliustikuga. Vanuseliselt osutusid nooremaks läänepoolsed veed, mis ilmselt viitab põhjaveeladestiku lääneosa suuremale avatusele liustiku eksisteerimise jooksul. Seda nägemust toetavad ka sulfaadi märksa positiivsemad $\delta^{18}\text{O}_{\text{SO}_4}$ väärtused põhjaveeladestiku lääneosas, mis kinnitavad raske atmosfäärse hapniku ($\delta^{18}\text{O}_{\text{atm}}$) mõju sealse sulfaadi tekkimisele.

PAPERS I-IV

CURRICULUM VITAE

Valle Raidla

Date of birth July 17, 1975

E-mail: valle.raidla@gi.ee

Education

- 2003–... University of Tartu, PhD studies, geology
2000–2003 Tallinn University of Technology, master studies, applied geology, MSc 2003
1993–1999 Tallinn Pedagogical University, bachelor studies, geoecology, BSc 1993

Career

- 2005–... researcher, Institute of Geology at Tallinn University of Technology
1999–2005 engineer, Institute of Geology at Tallinn University of Technology
1996–1999 technician, Institute of Geology at Tallinn University of Technology

Research activity

Degree information

Valle Raidla, Master's Degree, 2003, (sup) Enn-Aavo Pirrus, Rein Vaikmäe, Kambriumi-Vendi põhjavee süsiniku sisalduse formeerumine (Formation of carbon concentration in Cambrian-Vendian aquifer), Tallinn University of Technology, Faculty of Power Engineering, Department of Mining

Field of research

Dating with radiocarbon method, evolution of isotopic and chemical composition in natural waters.

Grants and Awards

- Stipendium from the Foundation Development Fund of Tallinn University of Technology in 2001;
- The first place in the competition of best research work by young geologists at The Geological Society of Estonia in 2003.

Current grants and projects

Application of isotopic and geochemical indicators in studies of global climate and environmental changes

LAPBIAT project: Nutrients in active layers of catchments of polar lakes in changing climate conditions

Professional development

First Regional Europe Workshop on Modern Trends in Liquid Scintillation Spectrometry. Held from June 16 to June 18, 2004. Karlsruhe, Germany.
Quantulus Customer Training Week. Held from May 7 to May 11, 2007. Turku, Finland

Important publications

- Raidla**, V., Kirsimäe, K., Vaikmäe, R., Jõelet, A., Karro, E., Marandi, A. and Savitskaja, L., 2009. Geochemical evolution of groundwater in the Cambrian-Vendian aquifer system of the Baltic Basin. *Chemical Geology*, 219–231.
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ELULOOKIRJELDUS

Valle Raidla

Sünniaeg: 17.07.1975.
E-mail: valle.raidla@gi.ee

Haridus

2003–...	Tartu Ülikool, doktorantuur geoloogia erialal
2000–2003	Tallinna Tehnikaülikool, magistrantuur rakendusgeoloogia õppesuunal, MSc 2003
1993–1999	Tallinna Pedagoogikaülikool, bakalaureuseõpe geoökoloogia erialal, BSc 1999.

Teenistuskäik

2005 – ...	Tallinna Tehnikaülikool, TTÜ Geoloogia Instituut; erakorraline teadur
1999–2004	TTÜ Geoloogia Instituut, insener
1996–1999	TTÜ Geoloogia Instituut, tehnik

Teadustegevus

Teaduskraadi info

Valle Raidla, magistrakraad (teaduskraad), 2003, (juh) Enn-Aavo Pirrus, Rein Vaikmäe, Kambriumi-Vendi põhjavee süsiniku sisalduse formeerumine, Tallinna Tehnikaülikool, Energeetikateaduskond, Mäeinstituut

Teadustöö põhisuunad

Dateerimine radiosüsinikumeetodil, loodusike vete isotoop- ja keemilise koostise kujunemine.

Saadud grandid ja tunnustused

- 2001, Sihtasutuse Tallinna Tehnikaülikooli Arengufond stipendium;
- 2003, I koht Eesti Geoloogia Seltsi noorte geoloogide parimate uurimuste konkursil.

Jooksvad projektid

- Isotoop- ja geokeemiliste indikaatorite kasutamine globaalsete kliima- ja keskkonnamuutuste uurimisel
- LAPBIAT projekt “Biogeensed elemendid polaarjärvede valgalade aktiivkihis kliimamuutuste tingimustes”.

Erialane enesetäiendus

- First Regional Europe Workshop on Modern Trends in Liquid Scintillation Spectrometry. 16.–18. juuni 2004. Karlsruhe, Saksamaa
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