

The origin of barium in the Cambrian–Vendian aquifer system, North Estonia

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Abstract. Identification of the barium occurrence and its origin is made on the basis of the groundwater chemistry study. High Ba content has been detected in the Cambrian–Vendian aquifer system in the coastal vicinity of the Gulf of Finland in Estonia and St Petersburg. The dissolution of Ba from witherite as the primary source was derived from the analysis of the aqueous solution equilibrium with Ba-related minerals. It is reflected in the chemical composition of groundwater and influenced by the galenite–calcite–fluorite polymetallic mineralization in Vendian sandstones. The dissolution and re-deposition of carbonates and baryte are confirmed by mineral saturation states for an aqueous solution and distribution of other species in the groundwater of the Cambrian–Vendian aquifer system in North Estonia.

Key words: groundwater chemistry, barium, fluoride, witherite, cation exchange, radium, Baltic Basin.

INTRODUCTION

Barium as a trace element in groundwater originates primarily from natural sources of water-bearing igneous and sedimentary rocks through the dissolution of barium-hosting minerals. The low solubility of barium-bearing minerals, especially baryte, inhibits the expansion of large amounts of barium in groundwater. However, regional studies of fresh groundwater in many countries have detected a high level of barium, for example, up to 10 mg/L in the USA (Calabrese 1977), up to 4.7 mg/L in Lithuania (Klimas 1988), up to 0.6 mg/L in Canada (Subramanian & Meranger 1984), up to 2.5 mg/L in the Netherlands (Van Duijvenboden 1989), and up to 20 µg/L in Sweden (Reeves 1986). High barium concentrations in deep groundwaters occur in sandstones of oilfields, exceeding several tens of mg/L, for example over 50 mg/L in the Rotliegendes Formation in Germany and up to 175 mg/L in the Carpathian Foredeep Meso-Cenozoic rocks (Kolodiy 1983; Traber 2002). The concentration of barium depends on the content of sulphates in groundwater, which is controlled by baryte solubility. A barium anomaly, with its concentrations ranging from 2 to 9 mg/L, has been revealed also in the Cambrian–Vendian aquifer system in North Estonia (Otsa & Tamm 1997).

In general, the barium content in drinking water is not regulated by directives or drinking water standards. Only the Environmental Protection Agency

of the USA (US EPA) has limited the barium content in drinking water to the level of 2.0 mg/L and the Russian authorities to 0.1 mg/L (SanPiN 1996). The World Health Organization (WHO) has published a guideline value of 0.7 mg/L for groundwater suppliers (US EPA 1995; WHO 1996). For that reason, quite little attention has been paid to barium hydrochemistry in the hydrogeological literature.

High barium concentrations are found in the groundwater used as drinking water in the northern part of the Baltic Basin in the Estonian and St Petersburg coastal area (Fig. 1). During the last years some studies have been performed on the Ba occurrence in Estonian groundwater (Karro & Marandi 2003; Marandi et al. 2004). It has been supposed in previous studies that the high barium in Cambrian–Vendian groundwater results from the upward migration of Ba from the underlying weathered crystalline basement. However, the authors do not discuss the solubility potential of basement minerals, which could produce the high barium concentration into the overlying Cambrian–Vendian aquifer system. This might not be the only reason for high barium content, because elevated concentrations of Ba have been detected in other aquifers in the Baltic Basin, which have no hydraulic connection with the crystalline basement. For example, in the Upper Eifelian–Givetian terrigenous aquifer system in Lithuania the barium content varies from 0.3 to 1.8 mg/L (Klimas 1988). In the St Petersburg region

maximum Ba concentrations are 2.7 mg/L in the groundwater of Ordovician limestones, 1.7 mg/L in Ordovician–Cambrian and Devonian sandstones, and 0.9 mg/L in Quaternary sediments. Besides, groundwaters in the crystalline rocks of Finland contain only traces of barium, which do not exceed a few tens of micrograms per litre (Backman et al. 1999). So, the similarity of basement rock facies in Finland and Estonia allows us to assume that the basement weathering core cannot be the only source of barium anomaly in the northern Estonian coastal area. Thus, the identification of the sources of barium anomaly in groundwater is still topical.

MATERIALS AND METHODS

The aim of the study was to collect and analyse previously published material on barium hydrochemistry, and to use new interpretation methods of groundwater chemistry data in order to assess and define the origin of barium anomaly in the Cambrian–Vendian aquifer system. All available data were incorporated into the water chemistry database to draw up a more comprehensive vision of the groundwater chemistry formation by using qualitative thermodynamic analysis of aqueous solutions. The objectives of the study are (1) to delineate the extent of Ba-rich groundwater in the various aquifer units and in basement rocks, (2) to analyse the thermodynamic equilibrium of groundwater with different minerals and reveal its effects on the groundwater chemistry, and (3) to assess the distribution of radium isotopes in groundwater and its relation with barium occurrence.

The equilibrium thermodynamics of groundwater was studied by using PHREEQE (Parkhurst et al. 1980), which calculates the saturation states for an aqueous solution relative to carbonate minerals and other species. Laboratory determinations of barium were performed by atomic absorption spectroscopy (Perkin-Elmer model 5000) in the laboratory of the Estonian Environmental Protection Agency.

REGIONAL HYDROGEOLOGICAL FRAMEWORK

The Estonian basement is covered by sedimentary rocks of Vendian–Devonian age and overlain by the Quaternary cover (Fig. 2). The Cambrian–Vendian (C–V) terrigenous aquifer system, which is the most important source of water supply in northern Estonia, lies directly on the crystalline basement rocks. On the basis of lithologic-stratigraphical and hydrogeological properties the Vendian and Cambrian rocks are divided into two aquifers and two confining units. The Gdov (V₂gd) and Voronka

(V₂vr) aquifers are separated by the Kotlin (V₂kt) aquitard. The Lontova (C₁ln) confining unit overlies the Cambrian–Vendian aquifer system in the whole Estonia and practically inhibits the infiltration of precipitation, leakage from streams, and groundwater flow from other overlying Palaeozoic aquifer systems. The Gdov aquifer consists of sand- and siltstones with the thickness of 40–100 m and lies directly on the basement. The Gdov aquifer is covered by the clayey 50–70 m thick Kotlin Formation in eastern Estonia. The Voronka aquifer consists of variable siliciclastic rocks – argillaceous to quartzose sandstones and siltstones. The thickness of the Voronka aquifer is 10–40 m in the Estonian Homocline.

The Cambrian–Vendian aquifer system is covered by 50–100 m thick Cambrian clays that form the laterally continuous Lontova aquitard. The aquifer system crops out in the bottom of the Gulf of Finland. The highest groundwater pressure zone is in the southern part of Estonia and groundwater discharge is towards the Gulf of Finland. The hydraulic conductivity of aquifers on the Estonian Homocline varies within 0.5–13 m/d and transmissivity within 25–1000 m²/d. These values are much higher in the coastal zone than in the southern part of Estonia. The vertical hydraulic conductivity values were derived through the calibration of a digital Cambrian–Vendian groundwater flow and MT3D models (Mokrik & Mažeika 2002; Mokrik 2003). The vertical hydraulic conductivity of the confining units ranges from 4×10^{-7} to 5×10^{-6} m/d and leakage from 10^{-8} to 10^{-6} L/d.

Glacial activities during the Pleistocene have formed erosional valleys, which cut through the Lontova aquitard and are filled with glacial deposits in northern Estonia. These sediments, mostly tills, have hydraulic conductivity from 10^{-2} to 10^{-4} m/d. The porosity of aquifers changes laterally and within vertical sequences between 5% and 12% because of considerable variations in rock lithology.

The local groundwater flow on the Estonian Homocline follows from the regional flow pattern. During the Pleistocene the regional compaction-driven brine flow from the Moscow Basin was diluted by glacial meltwater and interglacial seawater (Mokrik 2003). The least mineralized groundwater is spread in the coastal area where the main meteoric recharge took place during the last glacial period, and in general the groundwater salinity increases with depth towards the south and east. The dissolution of silicates and carbonate cement of water-bearing rocks or precipitation of secondary minerals are evolved in the aquifer system closed to modern carbon dioxide gas. Calcium–sodium cation exchange and halite dissolution processes, which give rise to relatively mineralized water, are important. Physical-chemical parameters of the aquifer system indicate that a strongly reducing environment exists, except in the vicinity of

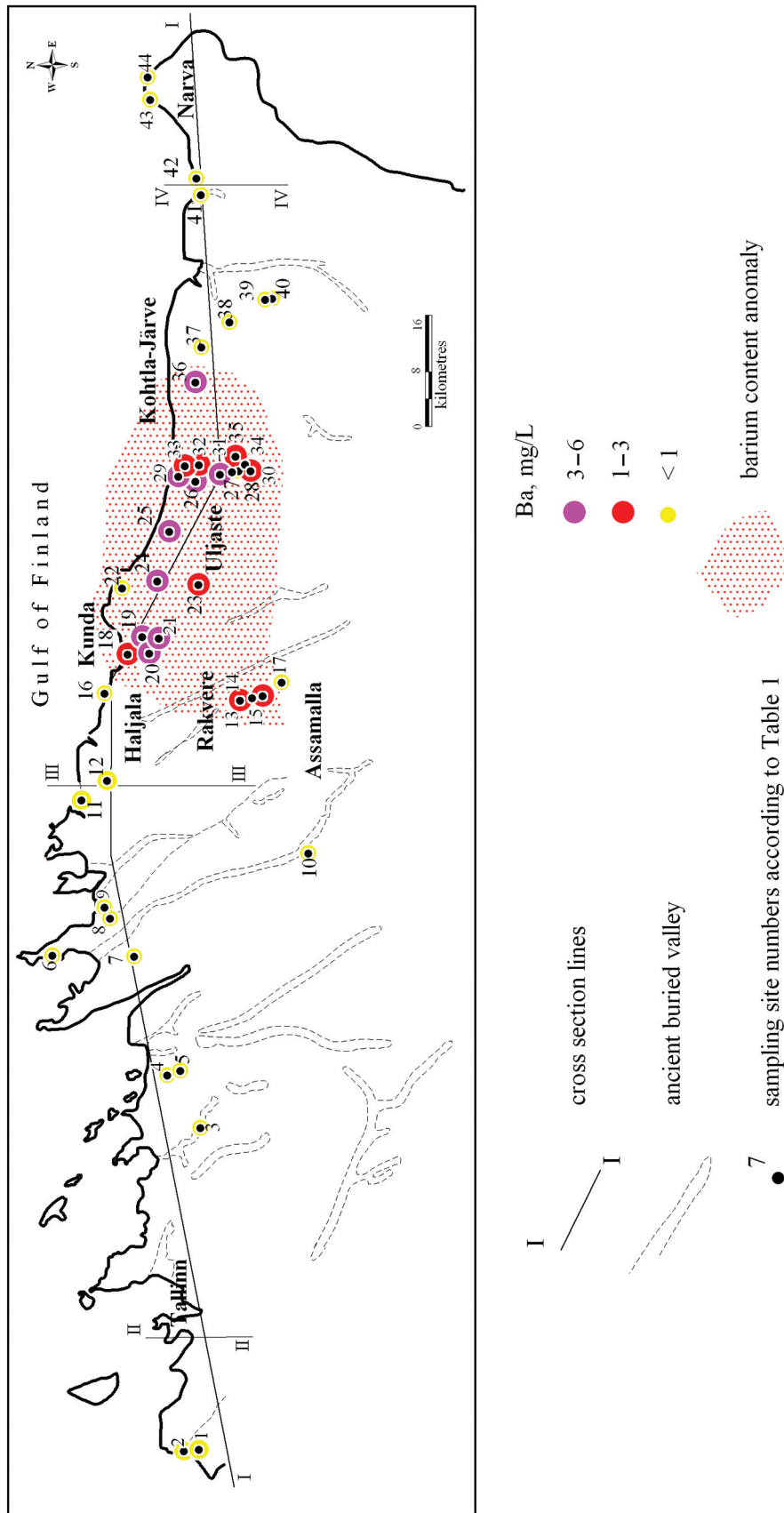


Fig. 1. Distribution of the Ba content in the Cambrian–Vendian aquifer system of the study area (based on Karro & Marandi 2003).

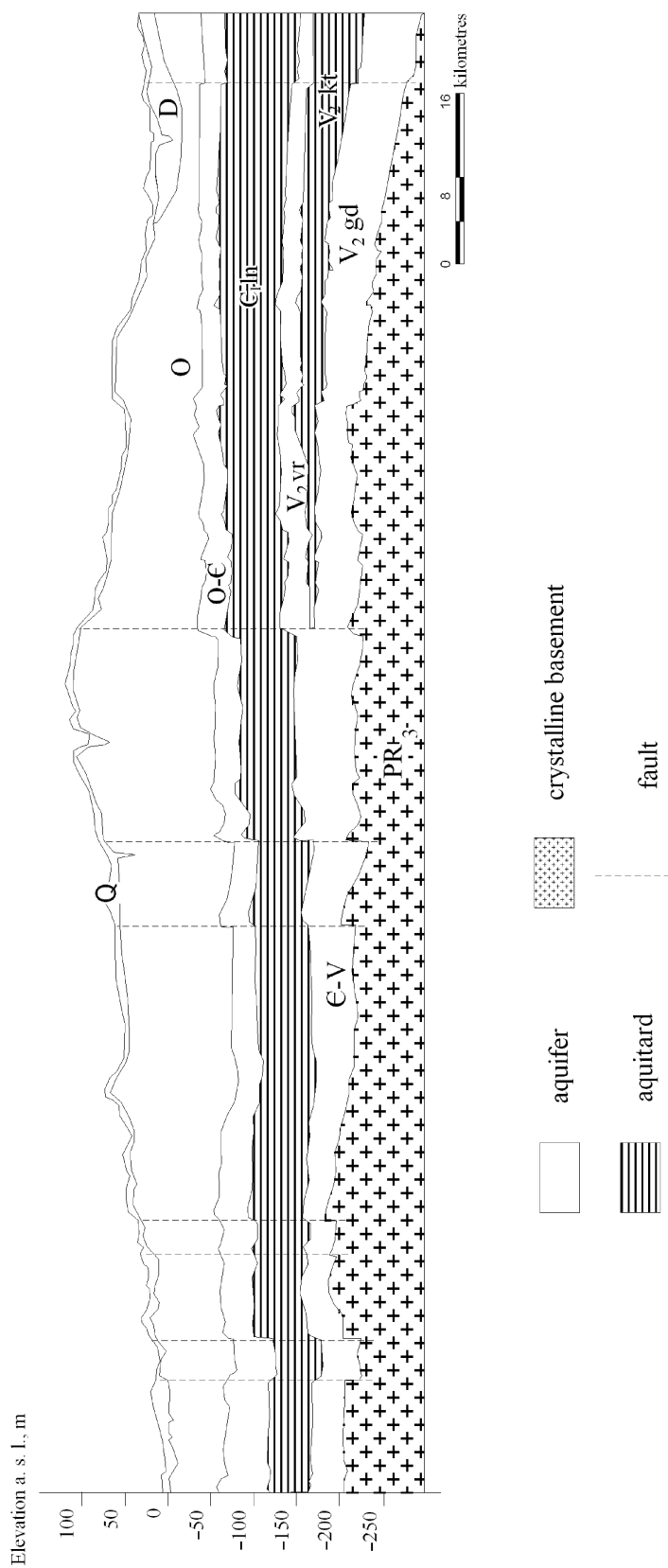


Fig. 2. Geological cross section I–I in the study area (based on Karro & Marandi 2003). Abbreviations used in Figs 2–11 and 13–15: Q, Quaternary aquifer system; D, Devonian aquifer system; O, Ordovician aquifer system; O–C, Ordovician–Cambrian aquifer system; C–V, Cambrian–Vendian aquifer system; V_{2vt}, Voronka aquifer; V_{2gd}, Gdov aquifer; C_{1ln}, Lontova aquitard; V_{2kt}, Kotlin aquitard; PR₃, Palaeoproterozoic.

ancient buried valleys, where the leakage of modern water occurs. The chemical composition of the Cambrian–Vendian aquifer system is very variable and is expressed by mean ions as follows (by decreasing succession in milliequivalent percentage; in brackets – the average Ba content in mg/L): $\text{HCO}_3\text{--Ca}$ (0.1), $\text{HCO}_3\text{--Ca--Mg}$ (0.3), $\text{HCO}_3\text{--Ca--Cl--Na}$ (0.16), Na--Cl--HCO_3 (sodium type – 0.84), $\text{Cl--Na--HCO}_3\text{--Ca}$ (3.1), and Na--Cl (0.28) composition. Outside the Estonian territory, in the Moscow Basin, Na--Ca--Cl and Ca--Cl type brines are prevalent.

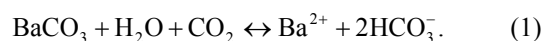
RESULTS AND DISCUSSION

The concentration of barium in the Cambrian–Vendian aquifer system was measured in 44 wells, where the mean and maximum contents were 1.8 and 6.37 mg/L, respectively (Table 1). In general, the sources of barium in groundwater can be barium-rich feldspars, plagioclases, micas, apatite, baryte, barium-carbonate minerals of the aragonite group, such as witherite and alstonite (= bromlite, barytocalcite), barium rare-earth uranium carbonates, etc. The barium content of world groundwaters is low, because barium-containing minerals have very low solubility in underground aqueous solutions. The concept of the earlier researchers (Karro & Marandi 2003; Marandi et al. 2004) for Estonia that basement rocks are the main source of barium in the Cambrian–Vendian aquifer system is negotiable, because Ba concentrations in the basement rock water of Finland and Sweden are below 0.1 mg/L (WHO 1990; Backman et al. 1999). The distinctly elevated barium concentration area in the Cambrian–Vendian aquifer system is limited by the Kunda, Rakvere, and Kohtla-Järve region near the southern coast of the Gulf of Finland (Figs 1–3). It is noteworthy that in the same place the Haljala–Vanamõisa hydrothermal polymetallic ore of galenite–calcite–fluorite mineralization has been revealed, which is located directly within Vendian sandstones (Raudsep 1997). An analogous sandstone-hosted galena–calcite–fluorite mineralization zone is found in the Laisvall area in northern Sweden, where galena, calcite, and baryte act as cementing agents in Vendian and Lower Cambrian sedimentary rocks. Calcite and dolomite minerals together with fluorite are reported as fracture fillings in the Rapakivi-like batholites and all of them are related to the Caledonian Deformation Front around the Baltic–Scandinavian Region. The radiometric ages of the galenite–calcite–fluorite mineralization here are close to 410–430 Ma and fluid inclusion investigations of veins indicate depositional temperatures of 100–150 °C (Alm et al. 2005).

The same hydrothermal ore mineralization was distinguished in Vendian sandstones in eastern Lithuania,

where exclusively high trace element, such as Ba, Cu, Sr, Sc, Pb, Ti, Mn, Y, Yb, etc., concentrations were determined. Here the barium content in Vendian sandstones is 670 mg/kg, gravelites 475 mg/kg, aleurolites 425 mg/kg, argillites 410 mg/kg, and maximally in sandstones up to 12 000 mg/kg (Kadūnas et al. 2004). This is significantly higher (up to one order more) as compared to other sedimentary formations in the Baltic Basin. However, the barium contents of 650–1000 mg/kg have been detected in the basement rocks, but the average concentration is some hundreds of ppm (Koljonen 1992; Koppelmaa & Kivisilla 1997). Taking into account that the underground leaching of weathered crystalline rocks is very limited, there is no potential for the migration of the large amounts of barium to the above-lying Cambrian–Vendian aquifer system. Thus, the ore mineralization phenomenon in the deposits of the Vendian Formation will explain the origin of barium in the groundwater of the Baltic region. Obviously, the Vendian Formation sandstones themselves as stratiform (bedded) Ba-rich sediments are the main source of barium in the groundwater of the Cambrian–Vendian aquifer system.

The overall baryte solubility is very low. However, to a certain extent, baryte can dissolve under conditions of sulphate depletion in the methanogenesis zone, leading to a high methane and barium content in fluids (Torres et al. 1996). On the Estonian Homocline the methane content is insignificant and baryte dissolution could not produce high barium concentrations into solution. It is commonly well known that barium carbonates have a much better solubility than the above-mentioned barium-related minerals. One of them is witherite, which usually forms in low-temperature hydrothermal conditions, like deposits associated with fluorite, baryte, calcite, aragonite, galena, and other sulphide minerals (Wedepohl 1978). Thus, witherite dissolution may cause enhanced barium values in the groundwater of the Cambrian–Vendian aquifer system according to the following alteration equation:



Although the solubility product values of calcite and witherite are very close, about $10^{-8.3}$ – $10^{-8.5}$ subjected from temperatures, witherite as a member of the aragonite group is less stable than calcite, and during dissolution its saturation in solution will not be reached. Vice versa, calcite, dolomite, and baryte are less soluble than witherite and can reach the saturation state during witherite dissolution in groundwater according to solubility product values. That is shown on the diagram based on the Cambrian–Vendian aquifer geochemistry data (Fig. 4). The Ba content increases by saturation. Witherite dis-

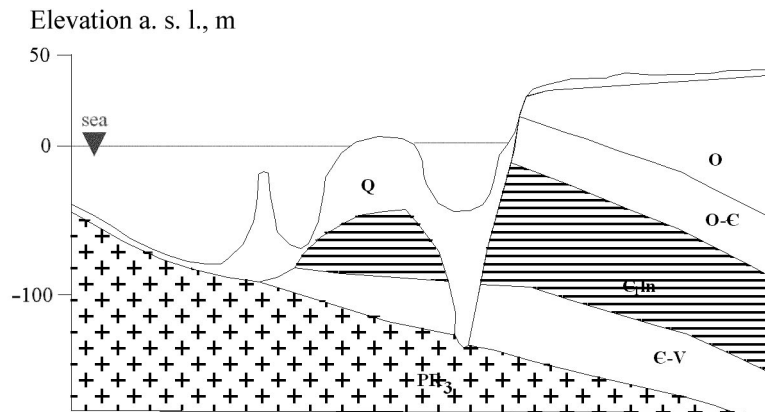
Table 1. Hydrochemical data of the Cambrian–Vendian aquifer system. Major and trace element contents in mg/L. ²²⁶Radium content in Bq/L. Eh value in mV. V₂vr, Voronka aquifer; V₂gd, Gdov aquifer; C–V, Cambrian–Vendian aquifer system (based on Karro & Marandi 2003). TDS, total dissolved solids

| Site | Aquifer | pH | Eh | TDS | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ | Ba ²⁺ | HCO ₃ ⁻ | SO ₄ ²⁻ | Cl ⁻ | ²²⁶ Ra | F ⁻ |
|------|-------------------|-----|------|------|------------------|------------------|-----------------|----------------|------------------|-------------------------------|-------------------------------|-----------------|-------------------|----------------|
| 1 | V ₂ gd | 8.3 | -13 | 224 | 30.0 | 8.5 | 34.0 | 7.0 | 0.20 | 103.7 | 22.0 | 62.0 | n.d. | 0.78 |
| 2 | V ₂ vr | 8.3 | 38 | 304 | 26.0 | 8.5 | 26.5 | 6.0 | 0.12 | 115.9 | 19.0 | 46.0 | 0.08 | 0.85 |
| 3 | V ₂ gd | 7.9 | 57 | 865 | 84.0 | 22.0 | 97.5 | 8.0 | 0.35 | 176.9 | 1.0 | 304.0 | n.d. | 0.45 |
| 4 | V ₂ vr | 7.8 | 78 | 1450 | 188.0 | 36.0 | 150.0 | 8.5 | 0.51 | 152.5 | 1.0 | 615.0 | 1.11 | 0.40 |
| 5 | V ₂ gd | 7.7 | 52 | 936 | 116.0 | 27.0 | 115.0 | 9.0 | 0.43 | 183.0 | 1.0 | 184.0 | 0.6 | 0.36 |
| 6 | V ₂ vr | 8.2 | -197 | 610 | 77.8 | 13.1 | 93.0 | 7.7 | 0.88 | 220.0 | 0.2 | 220.0 | n.d. | n.d. |
| 7 | C–V | 7.9 | -206 | 200 | 36.1 | 9.5 | 18.0 | 5.5 | 0.14 | 190.0 | 1.9 | 13.0 | n.d. | n.d. |
| 8 | V ₂ vr | 8.2 | -230 | 120 | 21.3 | 4.9 | 10.0 | 3.4 | 0.08 | 99.0 | 5.6 | 7.2 | n.d. | n.d. |
| 9 | C–V | 7.3 | -196 | 200 | 48.5 | 8.0 | 3.8 | 1.9 | 0.08 | 160.0 | 21.0 | 6.6 | n.d. | n.d. |
| 10 | C–V | 7.9 | -196 | 450 | 43.7 | 14.8 | 97.0 | 7.9 | 0.99 | 170.0 | 0.2 | 190.0 | n.d. | n.d. |
| 11 | V ₂ vr | 7.8 | -180 | 190 | 40.9 | 11.9 | 12.0 | 6.5 | 0.25 | 220.0 | 0.3 | 4.7 | n.d. | n.d. |
| 12 | V ₂ vr | 7.9 | 345 | 170 | 38.5 | 12.9 | 19.0 | 7.4 | 0.21 | 230.0 | 0.2 | 9.1 | n.d. | n.d. |
| 13 | V ₂ gd | 7.7 | -22 | 1020 | 88.0 | 24.0 | 128.0 | 10.0 | 2.41 | 201.3 | 1.0 | 345.0 | 0.9 | 0.91 |
| 14 | V ₂ vr | 7.7 | 88 | 396 | 34.0 | 16.0 | 98.0 | 8.5 | 0.77 | 201.3 | 1.0 | 150.0 | 0.5 | 0.52 |
| 15 | C–V | 7.8 | -221 | 500 | 60.6 | 18.7 | 100.0 | 8.6 | 1.50 | 180.0 | 0.5 | 220.0 | n.d. | n.d. |
| 16 | V ₂ gd | 7.9 | -204 | 380 | 41.3 | 12.4 | 92.0 | 7.9 | 0.82 | 210.0 | 0.2 | 140.0 | n.d. | n.d. |
| 17 | C–V | 7.8 | -220 | 530 | 56.5 | 17.7 | 100.0 | 7.9 | 0.79 | 180.0 | 0.2 | 220.0 | n.d. | n.d. |
| 18 | V ₂ vr | 8.0 | -242 | 330 | 35.7 | 14.1 | 66.0 | 8.0 | 2.10 | 320.0 | 0.2 | 29.0 | 0.66 | n.d. |
| 19 | V ₂ gd | 7.8 | 40 | 936 | 87.0 | 26.0 | 140.0 | 8.0 | 5.41 | 237.9 | 1.0 | 323.0 | n.d. | 0.96 |
| 20 | V ₂ gd | 8.3 | -30 | 866 | 80.0 | 26.0 | 130.0 | 8.0 | 6.08 | 262.4 | 1.0 | 323.0 | n.d. | 1.00 |
| 21 | V ₂ gd | 7.7 | -291 | 780 | 93.0 | 26.0 | 140.0 | 10.0 | 4.60 | 230.0 | 0.5 | 330.0 | 1.3 | n.d. |
| 22 | V ₂ vr | 7.5 | -329 | 260 | 63.8 | 16.5 | 4.8 | 4.1 | 0.46 | 290.0 | 2.6 | 6.0 | n.d. | n.d. |
| 23 | V ₂ vr | 7.7 | -180 | 330 | 65.0 | 17.0 | 27.0 | 8.5 | 2.30 | 340.0 | 12.0 | 10.0 | n.d. | n.d. |
| 24 | V ₂ gd | 7.8 | -216 | 660 | 75.4 | 20.9 | 120.0 | 9.2 | 5.90 | 240.0 | 0.2 | 250.0 | n.d. | n.d. |
| 25 | C–V | 7.8 | 159 | 658 | 61.1 | 23.0 | 115.0 | 8.5 | 3.77 | 242.8 | 2.0 | 220.0 | n.d. | 1.07 |
| 26 | V ₂ gd | 8.0 | 147 | 643 | 62.1 | 20.3 | 115.0 | 8.0 | 3.97 | 247.7 | 2.0 | 235.0 | 0.54 | 1.14 |
| 27 | V ₂ gd | 7.9 | -241 | 530 | 60.2 | 16.8 | 110.0 | 8.1 | 3.00 | 190.0 | 0.2 | 210.0 | n.d. | n.d. |
| 28 | V ₂ vr | 7.9 | -334 | 480 | 48.5 | 16.3 | 110.0 | 7.5 | 2.10 | 160.0 | 0.2 | 200.0 | n.d. | n.d. |
| 29 | V ₂ gd | 7.9 | -197 | 540 | 67.8 | 17.7 | 120.0 | 8.2 | 3.50 | 250.0 | 0.2 | 220.0 | 0.29 | n.d. |
| 30 | V ₂ vr | 8.2 | -212 | 420 | 22.5 | 7.3 | 140.0 | 6.9 | 0.77 | 190.0 | 0.2 | 180.0 | n.d. | n.d. |
| 31 | V ₂ gd | 7.9 | -201 | 450 | 54.1 | 18.2 | 110.0 | 7.9 | 2.40 | 180.0 | 0.2 | 210.0 | 0.27 | n.d. |
| 32 | V ₂ vr | 8.2 | -246 | 410 | 40.1 | 14.3 | 110.0 | 9.5 | 2.40 | 190.0 | 0.2 | 180.0 | n.d. | n.d. |
| 33 | C–V | 8.1 | -196 | 460 | 32.1 | 12.4 | 130.0 | 8.3 | 2.50 | 190.0 | 0.2 | 190.0 | 0.56 | n.d. |
| 34 | V ₂ gd | 7.9 | 124 | 576 | 42.3 | 15.8 | 130.0 | 7.5 | 0.81 | 183.6 | 2.0 | 231.0 | 0.16 | 0.86 |
| 35 | V ₂ vr | 7.9 | 129 | 640 | 44.3 | 16.9 | 130.0 | 7.5 | 0.74 | 151.3 | 2.0 | 233.0 | n.d. | 0.86 |
| 36 | V ₂ gd | 8.1 | 120 | 740 | 53.1 | 17.1 | 130.0 | 8.0 | 6.37 | 196.4 | 2.0 | 231.0 | n.d. | 0.92 |
| 37 | V ₂ vr | 7.9 | 81 | 696 | 56.1 | 9.1 | 200.0 | 7.0 | 0.83 | 150.1 | 2.0 | 316.0 | n.d. | 0.76 |
| 38 | V ₂ gd | 7.7 | -27 | 722 | 29.4 | 13.2 | 240.0 | 7.0 | 0.22 | 169.0 | 2.0 | 384.0 | 0.25 | 0.69 |
| 39 | V ₂ vr | 8.2 | -38 | 543 | 12.8 | 7.8 | 170.0 | 4.0 | 0.26 | 190.3 | 2.0 | 197.0 | 0.23 | 0.58 |
| 40 | V ₂ gd | 7.9 | 117 | 1531 | 57.3 | 28.4 | 375.0 | 9.5 | 0.10 | 161.0 | 2.0 | 700.0 | 0.21 | 0.66 |
| 41 | V ₂ gd | 7.8 | 101 | 1174 | 16.4 | 9.5 | 405.0 | 7.0 | 0.53 | 162.3 | 2.0 | 640.0 | 0.44 | 0.67 |
| 42 | V ₂ vr | 7.9 | 138 | 536 | 12.0 | 3.6 | 195.0 | 5.5 | 0.32 | 251.3 | 2.0 | 201.0 | 0.15 | 0.65 |
| 43 | V ₂ vr | 7.9 | -47 | 517 | 6.6 | 3.2 | 195.0 | 4.0 | 0.07 | 205.0 | 2.0 | 202.0 | 0.06 | 0.47 |
| 44 | V ₂ gd | 7.9 | -52 | 531 | 7.6 | 3.6 | 200.0 | 4.0 | 0.08 | 207.4 | 2.0 | 208.0 | 0.14 | 0.52 |

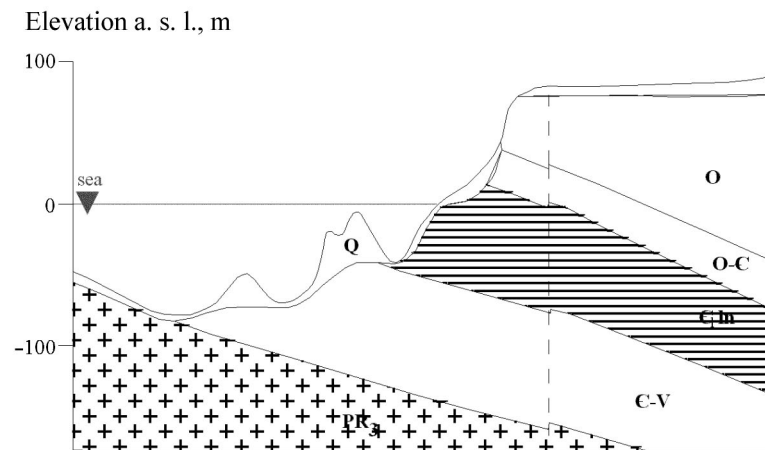
n.d., not detected.

solves when calcite (also dolomite) and baryte consecutively precipitate. During witherite dissolution and calcite precipitation the dissolved barium content in groundwater grows up to 6.37 mg/L (Table 1) and if barium concentration is suitably high, baryte starts to

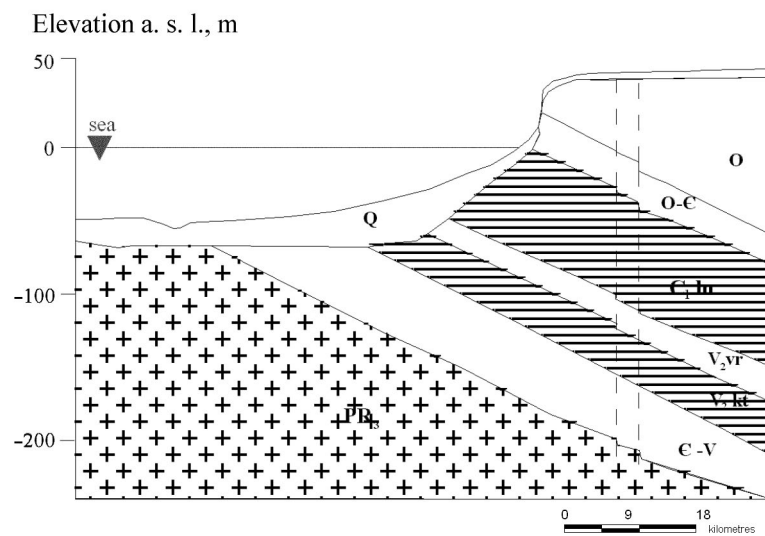
precipitate from the solution (Fig. 5). Saturation indices of baryte, witherite, and calcite versus the characteristic coefficient $\text{Na}^+ + \text{Cl}^-/\text{HCO}_3^-$ like the groundwater metamorphism degree (GMD) also demonstrate that by the decrease in the GMD only witherite is left in the sub-



Geological cross section II-II



Geological cross section III-III



Geological cross section IV-IV

Fig. 3. Geological cross sections II-II, III-III, and IV-IV in Fig. 1. For legend see Fig. 2.

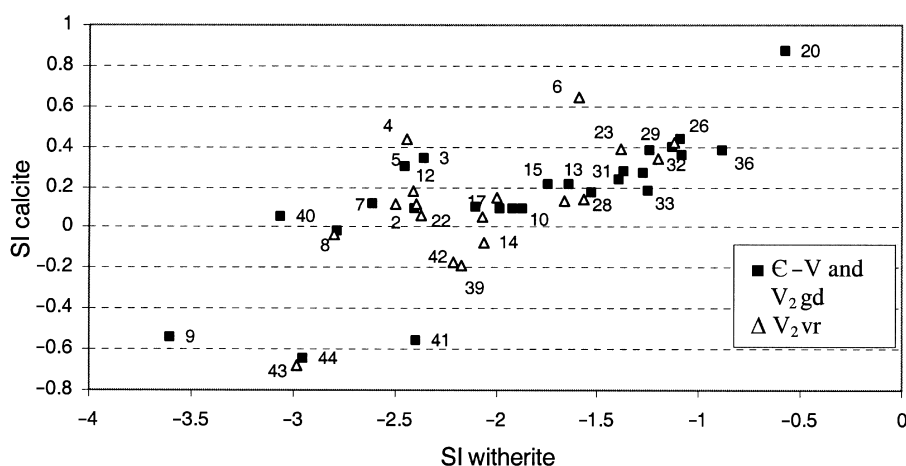


Fig. 4. Calcite and witherite saturation indexes (SI) diagram. Selected wells are denoted by numbers.

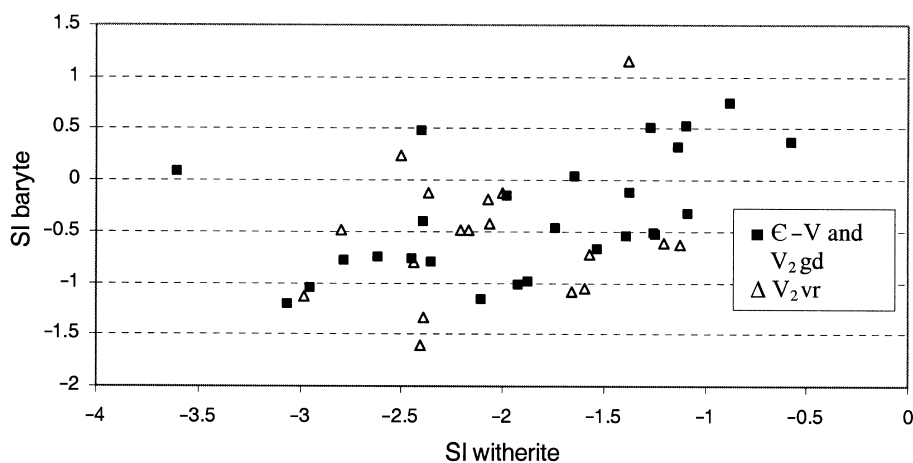


Fig. 5. Witherite and baryte saturation indexes (SI) diagram.

saturated state and is able to produce barium into water (Fig. 6). The characteristic coefficient $\text{Na}^+ + \text{Cl}^-/\text{HCO}_3^-$ reflects the salinization state or metamorphism of groundwater because sodium and chlorides are salt species and bicarbonate is a freshwater component (Mokrik 2003). Below values 2–5 of that coefficient calcite and baryte are supersaturated in the groundwater of the Cambrian–Vendian aquifer system. During witherite dissolution its solubility index is changed towards enrichment, and as a result Ba content rises in the aqueous solution (Fig. 7). At that time, when barium content exceeds 2.5 mg/L and sulphate content is around 2–4 mg/L, baryte precipitation starts. This indicates that baryte does not control the concentration of barium in groundwater. In the anomalously Ba-rich groundwater of Estonia the Ca^{2+} and Mg^{2+} concentration is high and pH ranges from 7.8 to 8.1. This shows that witherite dissolution

also leads to the precipitation of carbonates in the aqueous solution. Simultaneously, groundwater is subsaturated in respect of witherite. Outside the Haljala–Vanamõisa galena–calcite–fluorite mineralization zone groundwater has the barium content only up to 0.3 mg/L and belongs to the Na–Cl– HCO_3^- and Na–Cl or HCO_3^- –Ca–Cl–Na and HCO_3^- –Ca–Mg hydrochemical facies, which indicate, respectively, sub- or supersaturation with carbonates (calcite and dolomite). Groundwater, which is subsaturated in respect of calcite (dolomite) in the Voronka aquifer, is dominated by the Na–Cl– HCO_3^- and Na–Cl or Ca– HCO_3^- facies, which have the lowest barium concentrations, 0.16–0.28 and 0.1 mg/L, respectively. The former groundwater is the mixture of sodium-bicarbonate water with sodium chlorides in eastern Estonia, the latter is the groundwater in western Estonia, influenced by the percolation of meteoric water through

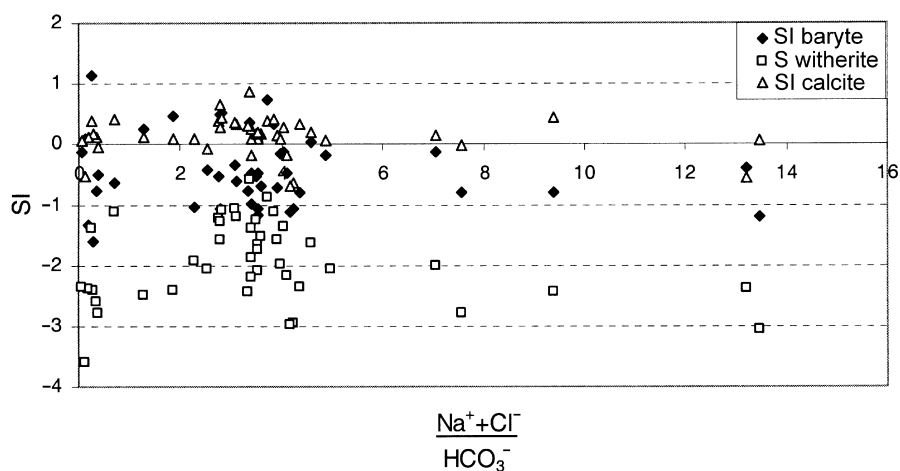


Fig. 6. Distribution of saturation indexes (SI) of baryte, witherite, and calcite for the characteristic coefficient $\text{Na}^+ + \text{Cl}^-/\text{HCO}_3^-$.

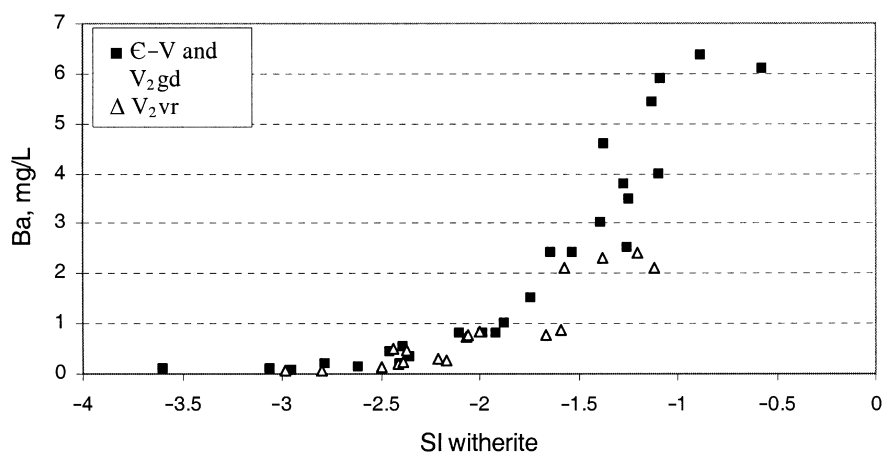


Fig. 7. Barium versus saturation indexes (SI) of witherite.

ancient buried valleys. In the regions where those groundwater facies occur, Ba-rich minerals are not represented in sandstones. In the case of supersaturation of the $\text{HCO}_3\text{-Ca-Cl-Na}$ facies with calcite, groundwater with a high barium content predominates. Barium-rich groundwater is formed in reduced environmental conditions and has elevated calcium, magnesium, bicarbonate, and chloride contents. Low-barium groundwater of the Gdov aquifer is also subsaturated with respect to calcite and dolomite. It is noteworthy that the barium content of groundwater is enhanced in the reducing environment except for some samples in the Gdov aquifer because of fluoride occurrence (see below) (Fig. 8).

The content on barium in groundwater is plotted against fluoride concentration in Fig. 9. Simultaneous dissolution of witherite and fluorite leads to some increase in fluoride concentrations in water, which is typical of

the galenite–calcite–fluorite mineralization zone. The fluoride content in the Gdov aquifer within the Haljala–Vanamõisa hydrothermal polymetallic area rises up to 1.14 mg/L and is controlled by relatively weak solubility of fluorite. The groundwater of the Cambrian–Vendian aquifer system is subsaturated in respect of fluorite and indicates the rise in fluoride content (Fig. 10). The excess fluoride content in hydrothermal ores compared to the adjacent area is about 0.3 mg/L. The ultimate fluoride concentration in groundwater depends on the long dissolution time of fluorite-bearing minerals, which in case of the Cambrian–Vendian aquifer system is up to 28–34 ky BP (Mokrik 2003). As a result, fluorite dissolves and fluoride and calcium concentrations increase according to the following reactions (Krainov & Shvec 1987):

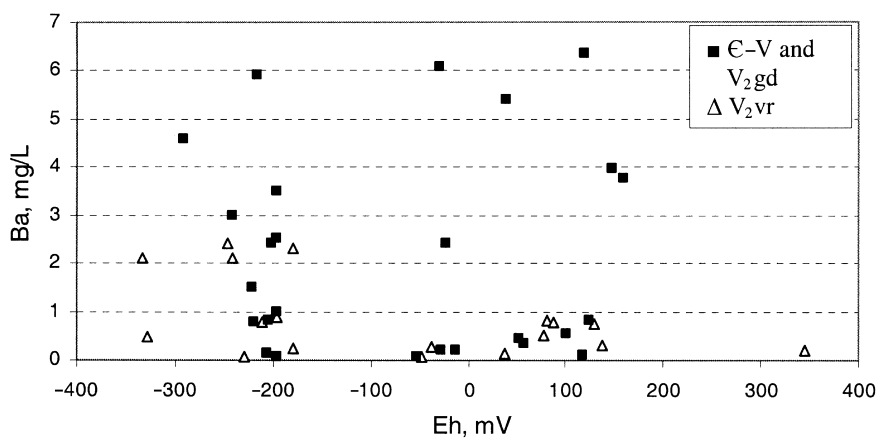


Fig. 8. Barium versus Eh diagram.

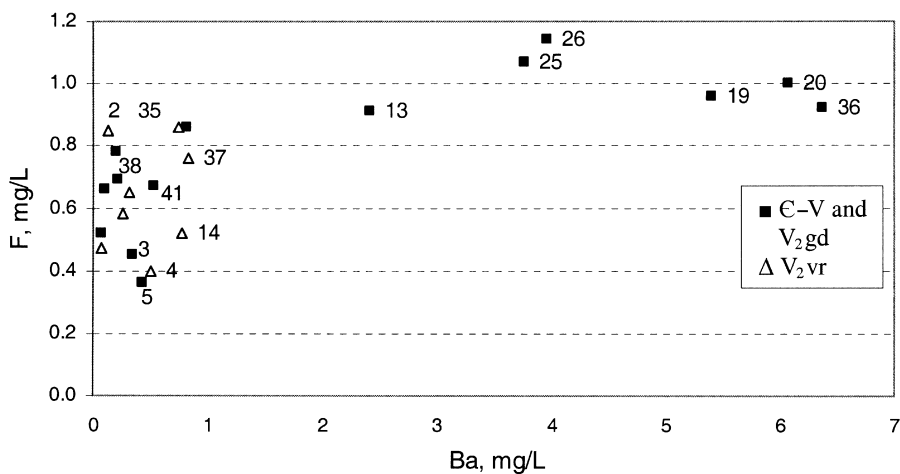


Fig. 9. Fluoride versus barium diagram. Selected wells are denoted by numbers.

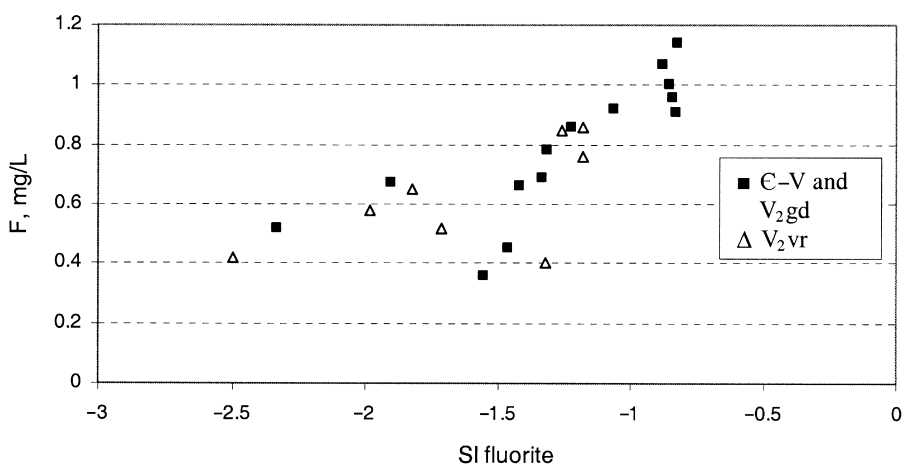
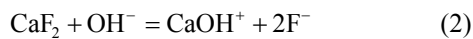
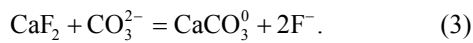


Fig. 10. Fluoride versus saturation indexes (SI) of fluorite diagram.



or



Calcium controls fluoride concentration during precipitation: the higher the fluoride, the lower the calcium content (Fig. 11). Calcium ion complexes significantly with carbonate ions, which results in the decrease in free calcium concentration and increase in the solubility of fluorite (Nordstrom & Jenne 1977). Ion exchange between sodium, calcium, and magnesium in groundwater can also influence the precipitation of calcite and limit fluoride solubility in groundwater. The cation (Na–Ca) exchange process is visible in the Piper diagram, where increased fluoride and barium values in groundwater are positioned in the plot of the carbonate deposition field (Fig. 12). The Na–Ca ion exchange has moved samples with enhanced barium and fluoride contents from the conservative fresh-saline groundwater line towards the upper corner of the Piper diamond. Different behaviour of calcium, magnesium, and sodium can be explained by cation exchange, because on the surface of clay fraction calcium ions are replaced by sodium and magnesium and as a result the Cl–Na–HCO₃–Ca type groundwater is formed. The comparison of the saturation indices of fluorite and witherite shows that both minerals are able to produce fluoride and barium into groundwater because of undersaturated states (Fig. 13). It is interesting that the trend slope declines sharply on the boundary of the saturation indexes –0.5 for witherite and –0.75 for fluorite. Up to this boundary the witherite saturation index is more negative than the fluorite index, but further the situation becomes contrary. Thus, the solubility properties of fluorite are limited by high calcium

concentrations, which are substantially enhanced during the cation exchange process.

It was also found that a relatively high ²²⁶Ra specific activity in groundwater (0.2–1.3 Bq/L) was in most cases in positive correlation with barium concentrations and total dissolved solid values (Fig. 14). The ²²⁶Ra isotope is the daughter product produced by alpha decay of ²³⁰Th in the ²³⁸U decay series. Radium occurs in groundwater through many processes including decay of parent isotopes, desorption, and ion exchange, dissolution of radium-bearing solids, etc. (Dickson 1990). Radium is soluble in the reduced environment and has a decreasing tendency towards the reduction–oxidation boundary due to complexes with carbonates or other minerals that include traces of radium during their deposition. The source rocks of radium may be related to clay minerals, radium-barium carbonates, and basement granites. Radium behaves similarly to divalent cations such as calcium and barium, and high content of radium is associated with high calcium and barium contents. Radium has a negative correlation with sodium and positive correlation with potassium (Fig. 15). The potassium content is highest in the Cl–Na–HCO₃–Ca type groundwater, with the average value of 8.5 mg/L. In the other groundwater types K concentration varies from 3.6 to 6 mg/L, except the Na–Cl facies with the average content of 7.6 mg/L. This could be related to the exchange of sodium to potassium on K-rich smectite-illite clays, from the surfaces of which radium is also desorbed. This mechanism may be real, because the concentrations dictated by uranium mineral equilibrium, aqueous uranium, and its daughter products are controlled only by sorption and ion exchange reactions at mineral surfaces (Taffet 2004). The Cambrian–Vendian aquifer system is represented by alternating sandy and

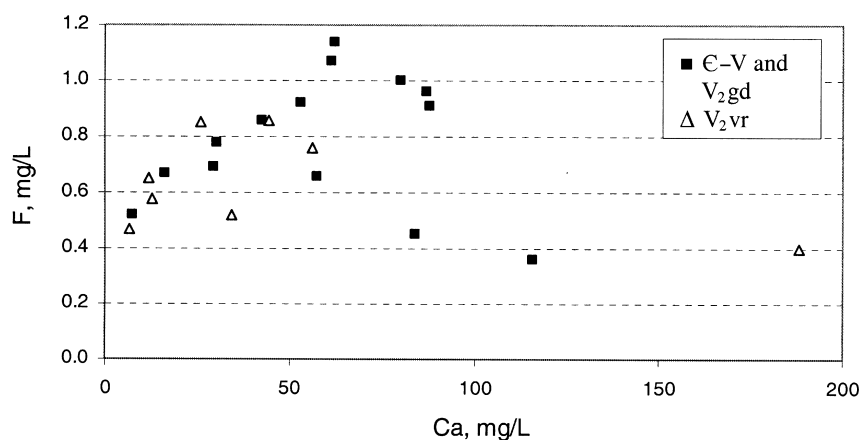
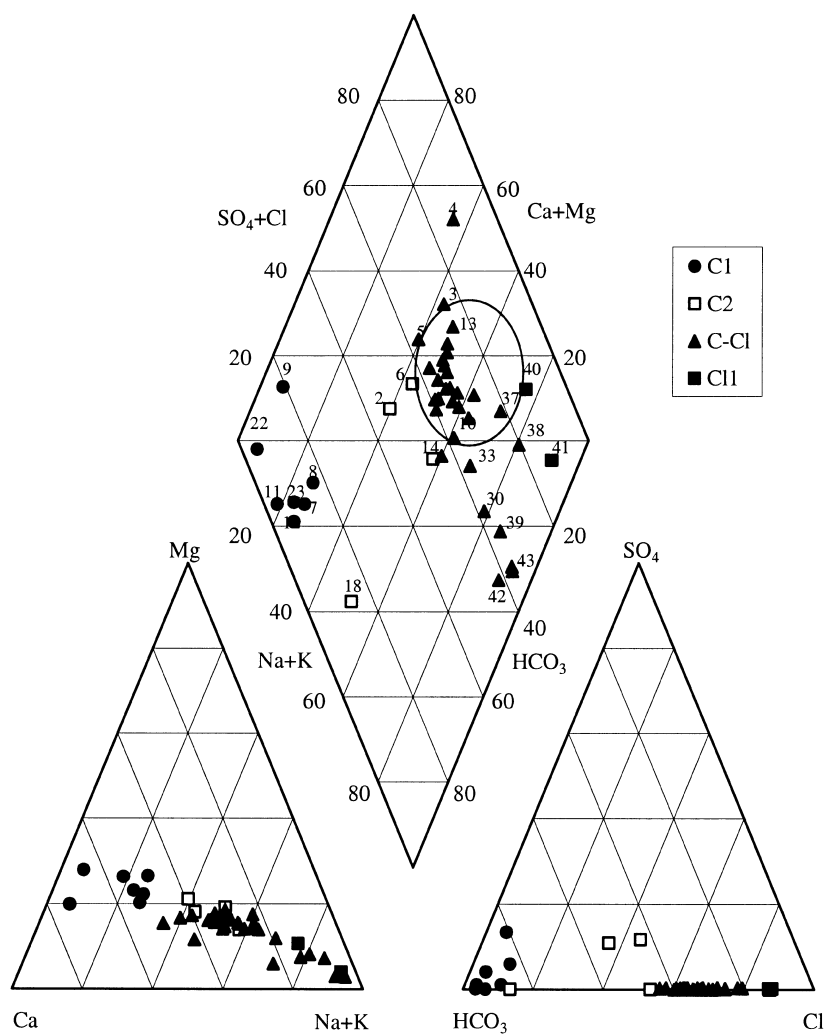


Fig. 11. Fluoride versus calcium diagram.



Groundwater types: C₁ (Ca-HCO₃), C₂ (Na-HCO₃), C-Cl (HCO₃-Cl), Cl₁ (Ca-Na-Cl)

Fig. 12. Piper diagram.

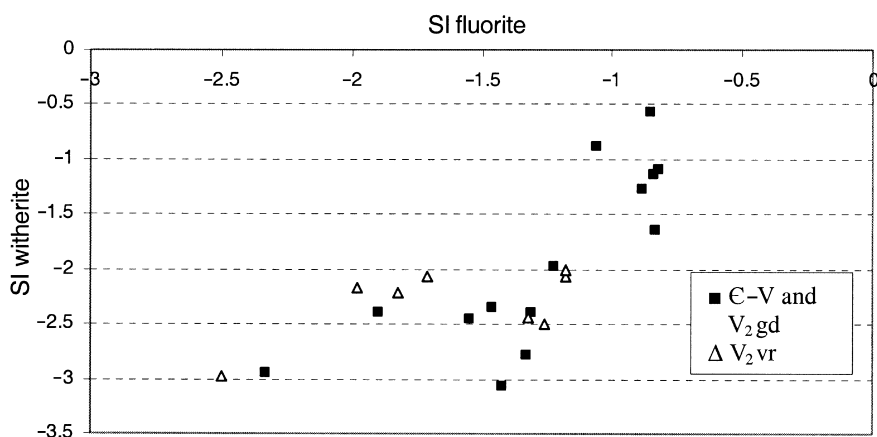


Fig. 13. Comparison diagram of saturation indexes (SI) of fluorite and witherite.

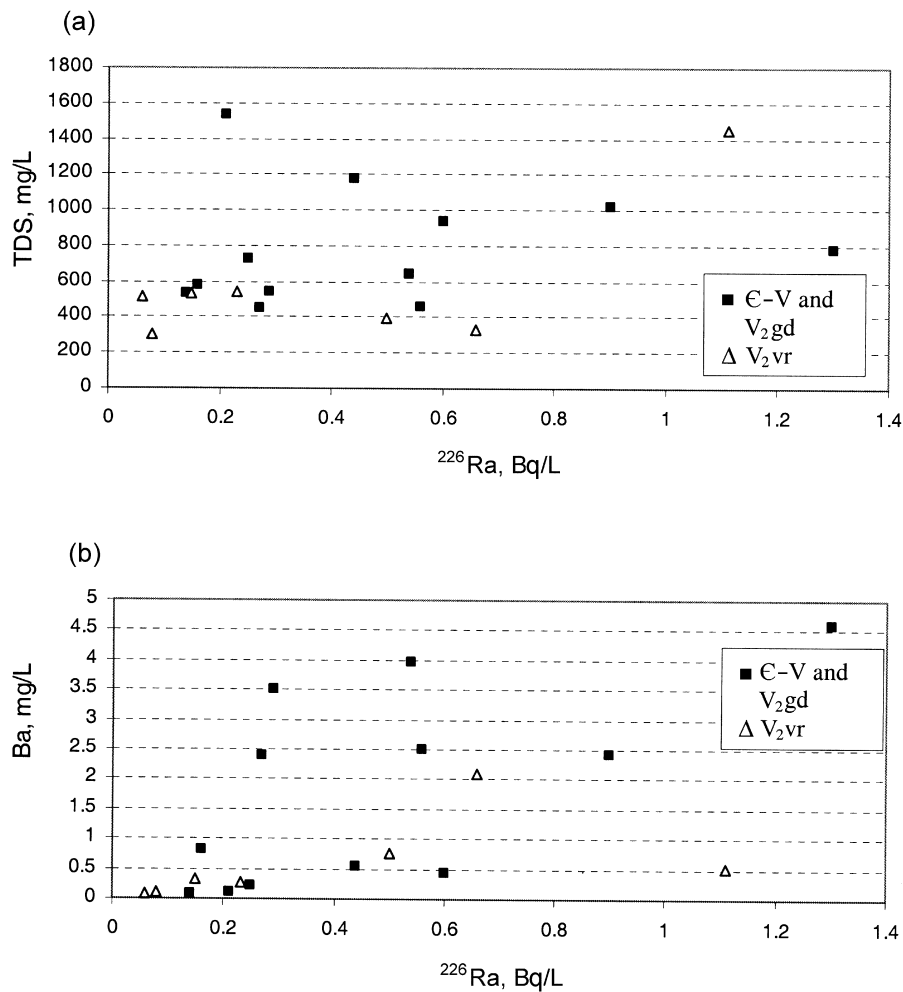


Fig. 14. Diagrams of total dissolved solids (TDS) versus ^{226}Ra (a) and barium versus ^{226}Ra (b).

argillaceous beds, whereas illite-smectite was formed in argillaceous matter. Such formation, as a rule, results in a release of silica and availability of potassium and aluminium, brought by groundwater solutions that had certain influence on the illitization of the smectite of Kotlin and Lontova clays (Mokrik et al. 2000). The main potassium-bearing rocks in the palaeoenvironment were highly radioactive Rapakivi-like granitic rocks.

SUMMARY AND CONCLUSIONS

Elevated barium and fluoride concentrations in the Cambrian–Vendian aquifer system of Estonia occur within Vendian sandstones in the Haljala–Vanamõisa hydrothermal polymetallic galenite–calcite–fluorite mineralization area. An analogous sandstone-hosted galena–calcite–fluorite mineralization zone is found in

the Laisvall area (Sweden), where galena, calcite, and baryte act as cementing agents in Vendian and Lower Cambrian sedimentary rocks. Mineralization occurs also in veins along fault zones. Hydrochemical studies of major and trace elements show that the probable barium source in groundwater is the dissolution of witherite. There is also a genetic relationship between fluoride and fluorite; the dissolution of fluorite is a source of fluoride in groundwater. Saturation indices show that while witherite and fluorite dissolve in an undersaturated aqueous solution, carbonates and baryte tend to precipitate. During carbonate precipitation an active cation (Na–Ca) exchange took place on the smectite–illite clay surface, which probably also controls radium desorption into groundwater. Major and trace element studies provide valuable information on the hydrochemical behaviour of elements in groundwater, but in the future the mineralogical and chemical composition of sandstones

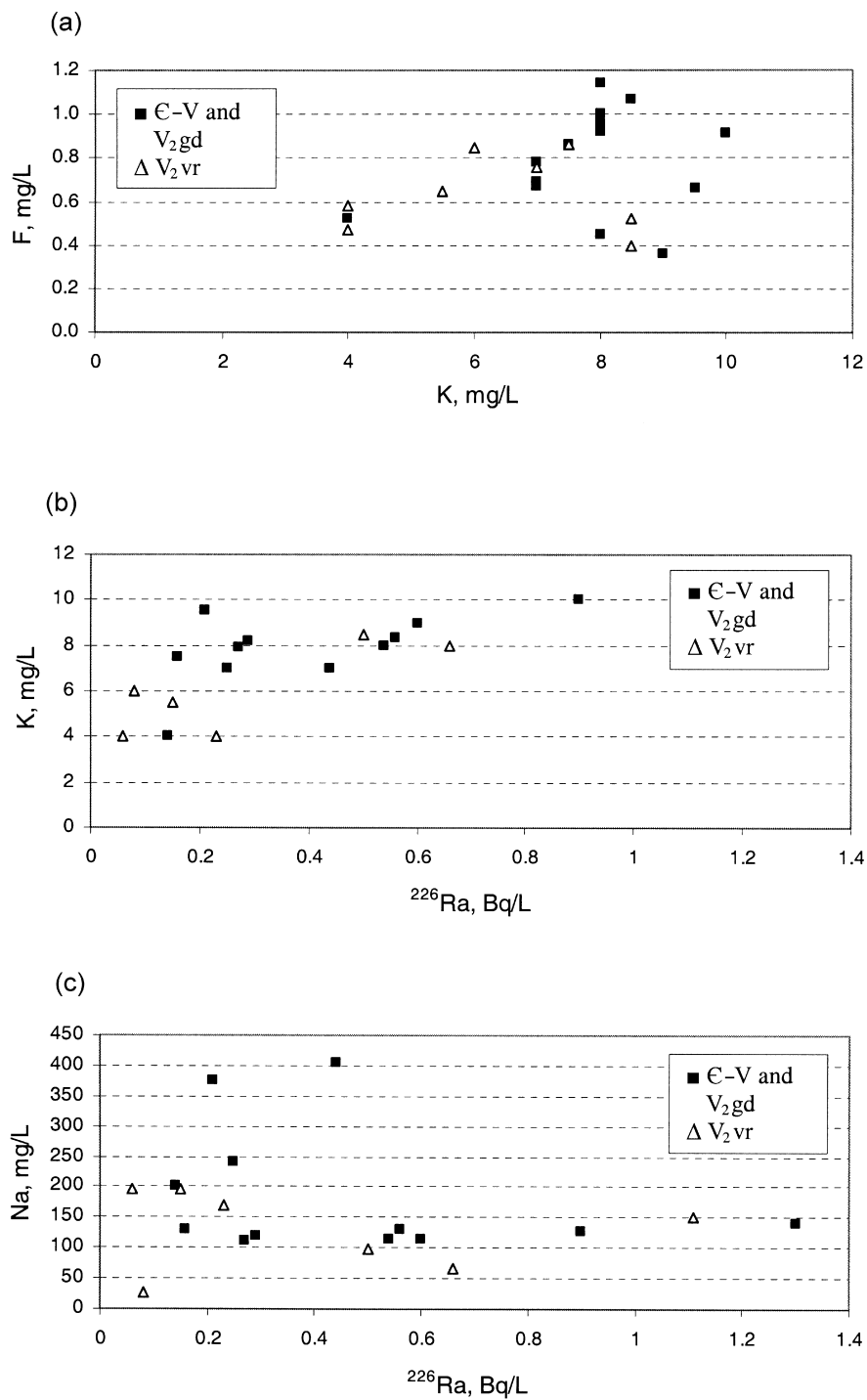


Fig. 15. Fluoride versus potassium (a), potassium versus ²²⁶Ra (b), and sodium versus ²²⁶Ra (c).

should be determined in order to assess the influence of the composition of host rocks on groundwater. The results of the present study give information on the mobility and contamination level of barium, fluorides, and radium in the groundwater of Estonia and St Petersburg district.

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Baariumi päritolu Kambriumi-Vendi veekompleksis Põhja-Eestis

Robert Mokrik, Enn Karro, Lehte Savitskaja ja Grazina Drevaliene

Kambriumi-Vendi veekompleksi kõrge baariumi ja fluoriidide sisaldused esinevad Haljala-Vanamõisa hüdrotarmaalse polümetallilise galeniit-kaltsiit-fluoriitse mineralisatsiooni piirkonnas. Põhjavee anomaalselt kõrge baariumisisaldus (kuni 6,37 mg/L) kontsentreerub Kunda, Rakvere ja Kohtla-Järve linnaga piirnevasse alasse. Looduslike vete baariumisisaldus on tavaliselt väike ja kontrollitud peamiselt barüüdi ning viteriidi lahustumisega. Põhjavees domineerivate hüdrogeokeemiliste protsesside analüüs, mis teostati arvutiprogrammi PHREEQE abil, näitas, et Põhja-Eesti Kambriumi-Vendi veekompleksi peamiseks baariumi geoloogiliseks allikaks on viteriidi lahustumine. Põhjavees esinevat fluoriidide sisaldust kontrollib mineraal fluoriidi ja vesilahuse vaheline keemiline tasakaal. Kui vesilahus on baariumi ja fluoriidide suhtes alaküllastunud, toimub viteriidi ning fluoriidi lahustumine. Samal ajal küllastub põhjavesi kaltsiidi, dolomiidi ja barüüdi suhtes, mis järk-järgult põhjaveest välja setivad. Karbonaatsete mineraalide väljasettimise käigus toimub savimineraalide ja vesilahuse vahel katioonvahetus (Na–Ca), mis arvatavasti kontrollib põhjavee raadiumisisaldust. Täpsustamiseks baariumi geoloogilisi allikaid, tuleks edaspidi põhjalikult uurida põhjavee keemilise koostise ja veekompleksi moodustavate kivimite mineraloogilise ning keemilise koostise vahelisi seoseid.