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Sulphur isotope composition of dissolved sulphate in the Cambrian–Vendian aquifer system in the northern part of the Baltic Artesian Basin

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ABSTRACT

The groundwater in the Cambrian–Vendian aquifer system with its $\delta^{18}O_{water}$ values of about −22‰ (VSMOW) and a low radiocarbon concentration is of glacial origin from the Last Ice Age. Earlier surveys have highlighted a negative co-variance of sulphate and bicarbonate content in the groundwater of the Cambrian–Vendian aquifer system, whereas the most depleted dissolved inorganic carbon $\delta^{13}C$ values have been measured mainly in groundwater samples with the lowest sulphate concentrations. In this paper we studied the origin of sulphate and the factors controlling the sulphur and carbon isotope geochemistry in the aquifer system. Direct sources of sulphate were not found, but relying upon $\delta^{18}O_{SO_4}$ measurements we suggest that the sulphate originates from oxidation of sulphide minerals whereas the $\delta^{34}S$ of the dissolved SO_4^{2-} in the groundwater is more enriched than the $\delta^{34}S$ of the surrounding rocks. We show that bacterial activity may have caused the enrichment of $\delta^{34}S$ of sulphate.

1. Introduction

The Cambrian–Vendian (Cm–V) aquifer system is a confined waterbody in western and north-western parts of the East-European Platform. In shallowly buried marginal areas of the aquifer system, particularly in northern part of the Baltic Artesian Basin, the groundwater is fresh and widely used in public water supply. The fresh groundwater at the northern margin of the basin has the lightest known oxygen isotopic composition in Europe ($\delta^{18}O_{water}$ values of around −22‰) and a low radiocarbon concentration suggestive of glacial origin of the water (e.g. Vaikmäe et al., 2001).

Raidla et al. (2009) showed that the groundwater from the Cm–V aquifer system is a mixture of three end-members — fresh glacial meltwater, relict Na–Ca–Cl brine and recent meteoric water. The mass-balance model of the carbonate system coupled with the modelling of radiocarbon age of the groundwater from the Cm–V aquifer system (Raidla et al., 2012) shows that the infiltration of the water occurred not earlier than 14,000 to 27,000 radiocarbon years ago, which is coeval with the advance and maximum extent of the Weichselian Glaciation in the area (Kalm, 2012).

In this paper we study the sulphur isotope composition in the groundwater of the Cm–V aquifer system at its northernmost margin in North-Estonia. Our goal is to reveal the origin of sulphate and the factors controlling the sulphur and carbon isotope geochemistry in the aquifer system's water and rock matrix, and to test evidence of bacterial activity in the aquifer system's hydrogeochemistry. Raidla et al. (2012) put forward a hypothesis that, although the origin of the degradable organic matter and sources of sulphate in the groundwater are virtually unknown, it is possible that the isotope system has been modified by bacterial activity, most likely via sulphate reduction.

2. The study area

The Cambrian–Vendian aquifer system is the shallow northern part of the Baltic Artesian Basin (BAB), which completely underlies the Baltic States and partly the border areas of Russia, Poland and Belarus. A large part of the BAB lies beneath the Baltic Sea. The Cm–V aquifer system encompasses the thick (up to 90 m) sequence of Ediacaran and Cambrian sandstones alternating with clays and silty clays (Fig. 1). The Ediacaran and Cambrian sedimentary rocks outcrop into the Gulf of Finland and to the bottom of the Baltic Sea. The aquifer system is confined by the underlying crystalline basement of the Palaeoproterozoic age and the overlying Lontova–Lükati aquitard, and the groundwater is under pressure. In the northeastern Estonia the aquifer system is divided by

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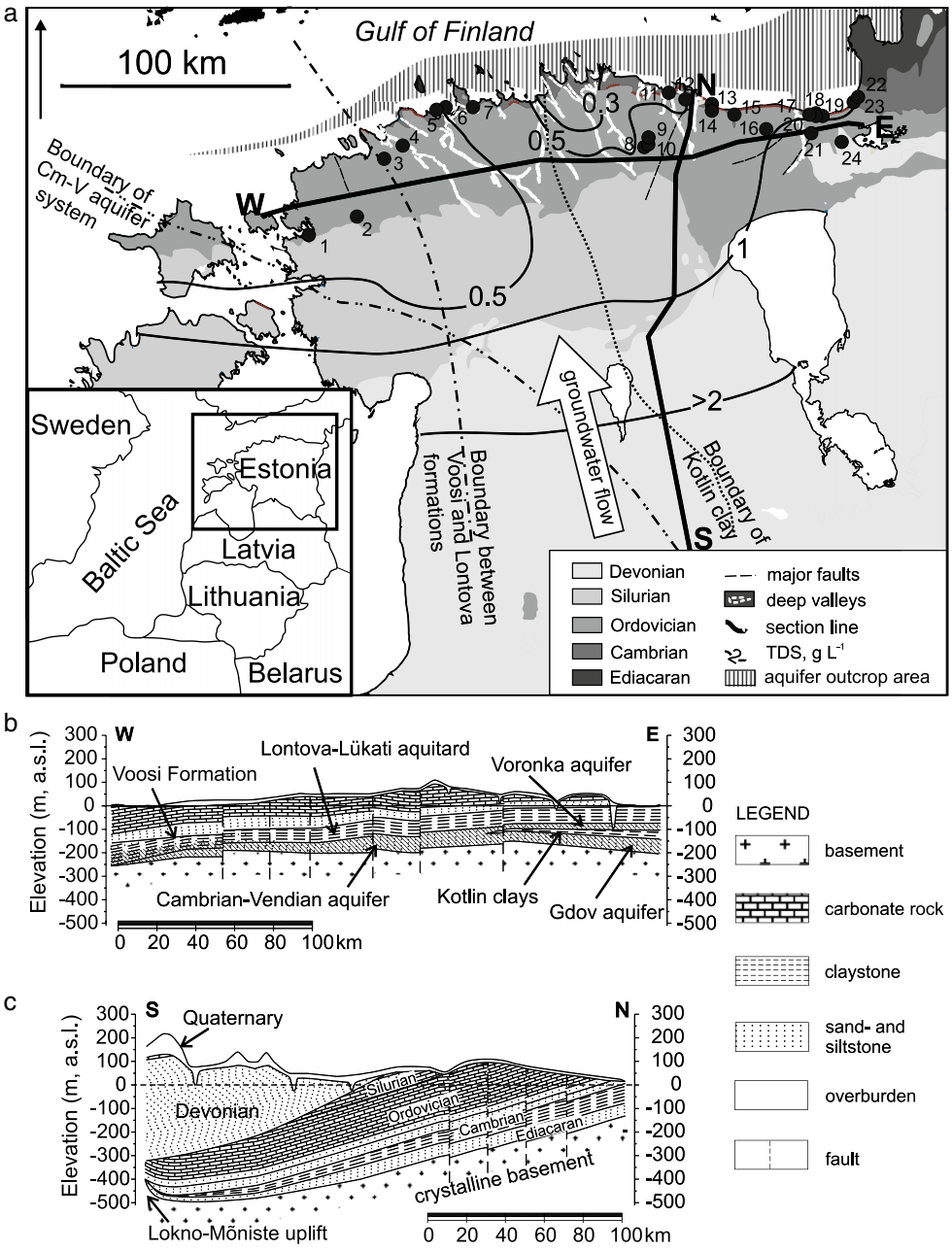

Fig. 1. A geological scheme of the northern Baltic Artesian Basin in Estonia with the positions of the studied wells (a), the West–East cross-section of northern Baltic Artesian Basin (b) and the North–South cross-section of the northern Baltic Artesian Basin (c).

Ediacaran clays of the Kotlin age into two aquifers: the upper Voronka (V_{2vr}) and the lower Gdov aquifer (V_{2gd}) (Fig. 1). In northern Estonia the conductivity of the water-bearing rock is 0.5 to 9.2 m d^{-1}, with the average of 5 to 6 m d^{-1}. Transmissivity in northeastern Estonia is 300 to 350 m^2 d^{-1}, decreasing in southerly and westerly directions (Perens and Vallner, 1997).

The Lontova–Lükati aquitard, overlying the aquifer system is composed of silty clays, siltstones and clays of the Lower Cambrian age. The Lower Cambrian clays are diagenetically immature and plastic with water content of about 20 to 30% (Kirsimäe and Jørgensen, 2000; Raidla et al., 2006). The thickness of the clayey complex is 90–100 m in North-Estonia, but decreases towards the south until disappearing in South-Estonia (Fig. 1). The aquitard has a strong isolation capacity with vertical hydraulic conductivity of 10^{-7} to 10^{-5} m d^{-1} (Perens and Vallner, 1997). The Lontova–Lükati clays are gradually replaced by interbedded clay and sandstone in western part of the area and their vertical hydraulic conductivity is $>10^{-5}$ m d^{-1} (Perens and Vallner, 1997). At the North-Estonian coastline the aquitard is incised by deep valleys filled with loamy till and glaciofluvial gravel (Tavast, 1997). These valleys serve as recharge areas where the water from the upper groundwater horizons infiltrates to the Cm–V aquifer system (Fig. 1). In the most part of northern and central Estonia, the siliciclastic rocks of the Cm–V aquifer system are covered by up to 300 m thick layer of Ordovician and Silurian marine carbonate rocks.

The groundwater in northern part of the aquifer system is of Cl–HCO_3–Na–Ca and Cl–HCO_3–Ca–Na type with the TDS content between 0.4 and 1.0 g L^{-1} (Savitskaja and Viigand, 1994). In southern part of the aquifer system the groundwater is replaced by saline relict Na–Cl water with TDS values of up to 22 g L^{-1} (Karise, 1997). The most characteristic property of the groundwater from the Cm–V aquifer system is its stable isotope composition. $\delta^{18}O_{water}$ values are between −18.5 and −22‰ VSMOW (Vaikmäe et al., 2001), whereas the isotope