GROUNDWATER RESIDENCE TIME AND PALAEOHYDROLOGY IN THE BALTIC ARTESIAN BASIN ISOTOPE GEOCHEMICAL DATA

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Abstract: A representative number of $^{14}$C analysis over the BAB area and the first $^{81}$Kr/Kr measurements from seven exploitation wells together with radiogenic $^4$He data were applied in order to study the potential influence glaciations deglaciations in the BAB area during the last several million years. Stable oxygen and hydrogen isotope values of $^{81}$Kr dated groundwater confirm that glaciations impact did not replace deep saline basinal brines with fresh and isotopically depleted meltwater over the all BAB area.

INTRODUCTION

The Baltic Artesian Basin with a surface of ~480,000 km$^2$ is one of the largest artesian basins in Europe. The BAB covers the territory of Latvia, Lithuania and Estonia, parts of Poland, Russia, and Belarus as well as a large area of the Baltic Sea, including the island of Gotland. Geologically the BAB is situated in the north-western part of the East European platform on the southern slope of the Fennoscandian Shield. The bedrock consists mainly of Ediacaran and Paleozoic sedimentary rocks overlying the Paleo-Proterozoic crystalline basement, which gradually slopes towards the south by 2-4 m/km. The thickness of the sedimentary cover reaches 5000 m in the south-western part, while the crystalline basement reaches the surface at the northern and south-eastern parts of the BAB. Hydrogeologically, the BAB is a complex multilayered system where the water in the sedimentary formation can be divided into 5 aquifer systems separated by 3 regional aquitards. General flow of the groundwater in the BAB is directed from southeast to northwest [1].
In most part of the deeply buried aquifer (>1000 m) the fluids within the system are represented by typical Na–Ca–Cl basinal brines (formation waters), which have salinities (total dissolved solids-TDS) of >1000 mg·l$^{-1}$. However, in shallowly buried marginal areas of the aquifer, particularly in the northern part of the Baltic Basin, where the aquifer forming rocks outcrop, the water is fresh (TDS<1000 mg·l$^{-1}$), drinkable and used for public water supply. Moreover in the northern margin of the BAB, the Cambrian-Vendian aquifer system (C-V) is the principal and most important source for the public water supply in Estonia. Earlier studies established that the groundwater in the northern part of this system has the lightest known isotopic composition in Europe ($\delta^{18}$O values from -18‰ to -23‰) [2,3]. These values are much more negative than the reported $\delta^{18}$O values of -10.4‰ for atmospheric precipitations in the area [2].

To explain this phenomenon it was proposed that during the late Weichselian the 500 to 1500 m thick Scandinavian ice sheet increased hydraulic pressure at the base of the glacier. The hydraulic gradient was at least 0.003, which is about one order of magnitude more than today and reversed the regional groundwater flow. This led to recharge of isotopically light glacial meltwater in Northern Estonia where the aquifer crops out. This occurred by drainage of aquifer system through tunnel valleys [3].

The age of the intrusion of glacial meltwater to the aquifer system has been constrained by a mass-balance model of the carbonate system coupled with the radiocarbon age of groundwater in the Cambrian-Vendian aquifer system, showing that the intrusion of the water occurred not earlier than 14000 to 27000 radiocarbon years ago [4]. This is coeval with the advance and maximum extent of the Weichselian glaciation in the area [5].

Before this work little data regarding groundwater residence time in the BAB, notably for brines in its deeper part has been available, except radiocarbon ages of intrusion of glacial meltwater [3,4,5]. Genesis and age of basinal brines (formation waters) have been estimated only from geological development of the area [8,9]. Based on the groundwater metamorphic degree (GMD), which characterizes the alteration of the groundwater chemical composition from the recharge area to the discharge area, it has been estimated that the age of deep formation waters in the southern part of BAB could be up to 60 Ma [6,7].

METHODS

For long the only available quantitative method for dating old ($5 \times 10^4$-$10^6$ a) groundwater was measurement of cosmogenic $^{36}$Cl (half-life 301 ka). Since the saline formation waters and brines in the deep aquifers of the Baltic Artesian Basin do not meet the restrictive criteria for the application of the $^{36}$Cl method, $^{81}$Kr (half-life 229 ka) is the only applicable isotope for radiometric dating. Recent developments in the ATTA method, based upon laser manipulation of neutral Kr atoms [10] have enabled the analysis of $^{81}$Kr in Kr gas extracted directly from groundwater samples using a tabletop apparatus, providing a practical approach for dating very old groundwater.

Samples were collected during three field campaigns ($^{14}$C, $^{81}$Kr campaign, and noble gas campaign). Wells were selected where radiocarbon was very low or could not be detected, based on earlier radiocarbon measurements. In Total, 7 wells were sampled: Two in Southern Estonia, two in Central Latvia and at three wells in Southern Lithuania. Two of the wells...
(Riga and Kemerī) are artesian; at the other wells, the installed submersible pumps were used for sampling.

The gas obtained by the degassing was analyzed for major gas composition on a quadrupole mass spectrometer before separating the Ar and Kr gases for further analysis. Krypton was extracted from the bulk gas at the University of Bern by cryogenic distillation and gas chromatography and the isotope ratios $^{81}$Kr/Kr and $^{85}$Kr/Kr were determined using the ATTA-3 instrument in the Laboratory for Radiokrypton Dating, Argonne National Laboratory. Based on the Atom Trap Trace Analysis method, ATTA-3 is a selective and efficient atom counter capable of measuring both $^{81}$Kr/Kr and $^{85}$Kr/Kr ratios of environmental samples in the range of $10^{-14} – 10^{-10}$. For $^{81}$Kr dating in the age range from 50 to 1,500 kyr.

Argon was also extracted from the bulk gas by cryogenic distillation. $^{39}$Ar activities were measured by low-level gas proportional counting at the Physics Institute, University of Bern. Based on Cl- and $\delta^{18}$O data, a mixing model with three end members was proposed [4]: brine, glacial meltwater and recent meteoric recharge. To accommodate the results from the deep samples, the chloride concentration of the brine end member needs to be increased from 20 g/kg to 100 g/kg, however. Based on the mixing model fractions of recent meteoric water, glacial meltwater and brine were determined. 4 of the 7 samples have a brine fraction of over 50%. On the other hand, Värska and Häädemeeste are mostly composed of recent and glacial waters. Ignalina and Klaipeda are not containing any glacial water. Ignalina, Klaipeda and Genziai are outside the range reachable by the mixing model. This leads to the unrealistic estimation of 18% glacial meltwater in Genziai. The deviations from the mixing model could be explained by mixing with seawater as a fourth end member (Klaipeda, Ignalina) or salt dissolution (Genziai).

DISCUSSION

The results from this study confirm the mixing model [4] with three end members: glacial meltwater with a lighter isotopic composition and high gas contents, recent meteoric water, and a saline, degassed brine. However, the deep samples from this study indicate a higher salinity for the brine end member (Cl- $\approx$ 90 - 110 g/kg, TDS $\approx$ 140 – 190 g/kg). The chemical signature suggests that the brine is up-concentrated seawater.

In Kemerī and Genziai, $^{81}$Kr concentrations are below the detection limit (R/Ra=0.02) indicating water that is older than 1.3 Ma. From this it was concluded that the age of the brine is beyond the dating range of $^{81}$Kr of 1.3 Ma and that subsurface production of $^{81}$Kr is negligible. Under the assumption that the glacial end member was recharged during the last glaciation, the $^{81}$Kr age of the recent meteoric component was determined (for some of the wells only a lower limit could be given). The $^{81}$Kr age of the meteoric component ranges from 176 to $> 900$ ka and generally increases in the direction of flow.

CONCLUSIONS

For the first time, the deeper part of the Cm-V aquifer across the entire BAB was sampled for dating tracers, noble gases and chemistry. Chemistry and noble gases confirmed that the mixing model [4] with three end-members (meteoric water, glacial meltwater, brine) is suitable for northern Estonia and can be applied to the deeper parts of the aquifer as well. With depth the brine end-member becomes increasingly dominant and a more accurate composition for the brine end-member was established.
$^{81}$Kr measurements all gave abundances less than half of today’s atmospheric abundance, confirming that groundwater in the Cm-V aquifer is indeed very old. For two samples, after correction for contaminated well casings using $^{85}$Kr, $^{81}$Kr abundances below the detection limit were found, indicating that these waters are older than 1.3 Ma. These are the first samples with a $^{81}$Kr abundance below detection limit, providing evidence that underground production is negligible. The absence of underground production in this case increases credibility that the still quite new $^{81}$Kr dating method is robust.

Based on the mixing model and $^{81}$Kr measurements, the age of the meteoric end-member could be estimated. These confirm the modelling results [1] giving an average horizontal velocity of 0.34 m/a between the recharge area and the Gulf of Riga. As the brine was found to be beyond the dating range of $^{81}$Kr, mean ages for the samples as a whole cannot be given, only lower age limits.

$^4$He and $^{40}$Ar/$^{36}$Ar measurements confirm the generally very high residence times of the waters. However, $^4$He and $^{40}$Ar were found to be controlled by a combination of several factors, which makes them difficult to interpret and prevents their use as dating tools. Because $^{36}$Cl would also be problematic in the BAB, $^{81}$Kr measurements provided a unique tool to better understand and constrain flow patterns in the Cm-V aquifer of the BAB.

REFERENCES