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# STABLE ISOTOPE AND NOBLE GAS CONSTRAINS ON THE GENESIS OF THERAPEUTIC WATERS IN SOUTHEAST POLAND

**László PALCSU[1], Gabriella KOLTAI[1,2], Anikó HORVÁTH[1], Ireneusz BARAN[3], Anna BARAN[3,4] & Stanisław HAŁAS[4]**

*[1]Institute for Nuclear Research, Hungarian Academy of Sciences, Bem tér 18/C, 4026 Debrecen, Hungary*
*palcsu.laszlo@atomki.mta.hu, horvath.aniko@atomki.mta.hu,*
*[2]University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria gabriella.koltai@uibk.ac.at*
*[3]The Bronisław Markiewicz State Higher School of Technology and Economics in Jarosław, 37-500 Jaroslaw, Poland*
*annabaran1212@o2.pl, ireneuszbaran@o2.pl*
*[4]Maria Curie-Sklodowska University, 20-031 Lublin, Poland stanislaw.halas@poczta.umcs.lublin.pl*

**Abstract:** Noble gas and stable isotope analyses can provide useful information on the origin of groundwater including residence time of different mixed components. This paper focuses on two unique therapeutic water areas of Southeast Poland (Horyniec Spa and Iwonicz Spa Lubatowka Spa). Groundwater from the well Róża-III in the Horyniec Spa is of purely meteoric origin and seems to be recharged in the Middle Holocene. The calculated recharge temperature based on dissolved noble gas concentration has been obtained to be 7.6±0.6 °C, which corresponds to recent mean annual air temperature. Stable isotope composition of Lubatówka and Iwonicz Spa waters demonstrate a high contribution of formation water enriched in heavy isotopes of oxygen and hydrogen. Water samples from Lubatówka are characterized by high helium concentration, $(1\text{-}6)\cdot10^{-6}$ ccSTP/g, exceeding 25-150 times concentrations observed in surface water The low $^{3}He/^{4}He$ ratios indicate crustal origin. Substantially low noble gas concentrations (Ne to Xe) were found in the water samples from Iwonicz Spa. Subsurface degassing might have happened in the Lubatówka aquifer due to the presence of large methane gas fields. The elemental and stable isotope composition of the waters points out that one of the end members in the mixing pattern is a formation water, i.e. the evaporated ancient ocean water of the Paratethys from the early Cenozoic Era. These waters and maybe to a certain extent waters from Lubatówka are mixtures of freshly recharged meteoric water and formation water, although the presence of the third component cannot be excluded. The mean residence time of the freshwater component present in therapeutic waters of Iwonicz region has been estimated to be up to 1-2 decades.

**Keywords:** therapeutic waters, genesis, noble gases, isotope hydrology, Poland

## 1. INTRODUCTION

The sulphur-rich springs of Horyniec and the mineral waters of Iwonicz Spa and Lubatówka have been used for therapeutic purposes for several centuries. The geological structure of Iwonicz Spa and Lubatówka area is well documented from drill cores used for carbohydrate research. Several studies have dealt with the hydrogeological structure of the area (Cwanek et al., 1985; Wdowiarz, 1985) and with the chemical and isotopic composition of water (Ciężkowski, 1996; Porowski, 2001; Porowski, 2006, Baran & Halas, 2011, Rajchel et al., 2011). The isotopic composition of sulphur regarding the springs of Horyniec Spa has been studied first time by Żuk et al., (1973) and later on by Baran & Halas (2010). This paper aims to determine the origin of the water bodies, the mean residence times and how different mixing components contribute to the evolution of therapeutic groundwaters used in the Horyniec and Iwonicz region. Besides the elemental composition of water, stable isotopes, noble gases including the $^{3}He/^{4}He$ isotope ratio, and tritium have been used in the present study to gain more information about the hydrogeology of these aquifers.

## 1.1. Geology of the study areas

The two study areas (Horyniec Spa; Iwonicz Spa and Lubatówka) are located in Southern Poland. Horyniec Spa is situated near the Cretaceous hills of the Roztocze Rawskie at the margin of the Carpathian Foredeep, near the Ukrainian border, while thermal springs of Iwonicz and Lubatówka are located in the Carpathians (Fig. 1). The Carpathian Foredeep covers the area located north of the Carpathian margin and is built up by Miocene deposits (Oszczypko, 1999).

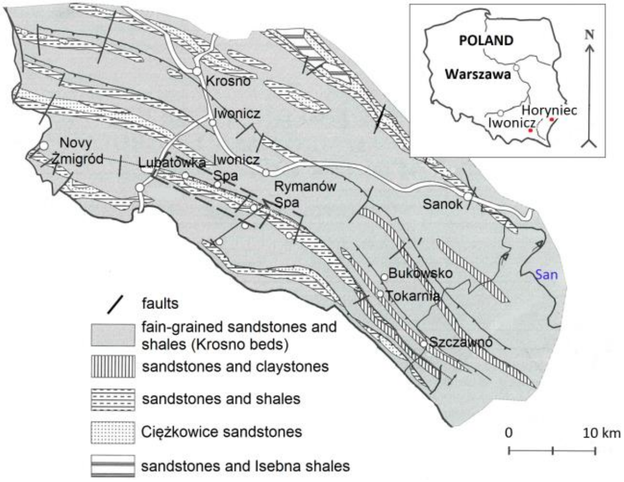

Figure 1. Location of Horyniec Spa and the geological structure of Iwonicz Spa – Lubatówka region, geological map modified after Poprawa & Nemcok (1989).

The formations are diversified both horizontally and vertically. The main rock complexes consist of gypsum, anhydrite and other evaporites. These sediments extend southwards both along and under the Carpathian thrust and northwards in the direction of Horyniec Spa (Dowgiałło 1969, Oszczypko 1981).

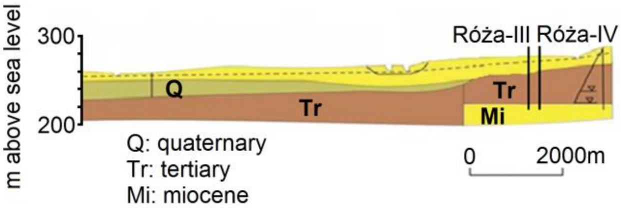

Figure 2. Geological cross-section of the Horyniec Spa region, modified after Meszczyński & Dziewa (2002).

The aquifer of Horyniec Spa is hosted in Miocene limestone, sandstone and sand deposits. The therapeutic groundwater is exploited by two wells: Róża III and Róża IV reaching depths of 29 m and 30.5 m, respectively (Baran & Hałas, 2010). By being a shallow basin, this area is filled with Neogene formations (lower Miocene limestones and gypsum, and upper Miocene clays) and a thin layer of Quaternary sediments (Fig. 2).

Mineral water wells in the Iwonicz Spa and Lubatówka area are situated in the Iwonicz anticline (Baran & Halas, 2011) that is comprised of Createous-Palaeogene flysch formations. The water-bearing zone is predominantly associated with gritstones and sandstones of a middle grain size, originating from shoals that are characterised by shale intervals. The aquifer is discontinuous as a consequence of the complicated geological structure that is rich in folds and faults. The initial Upper Cretaceous and Palaeocene shale and sandstone formations are altered as well. This nearly 500 m thick sandstone-shale complex can be divided into 4 bands (Fig. 3). The lowermost IV. Ciężkowice Sandstone formation consists of sandstone layers with different grain size and contains carbohydrates. Greenish-grey shales superimpose to these beds. The Palaeocene sequence ends with the III. Ciężkowice Sandstone complex overlaid by a thin variegated shale layer below the I. Ciężkowice Sandstone bands. The two sandstone layers do not differ significantly from each other, however, the II. Ciężkowice Sandstone contains less shale intercalations. From a hydrogeological point of view this area is characterized by low permeability. However, the large number of faults and folds generated by tectonic movements facilitates the infiltration of precipitation at certain places.

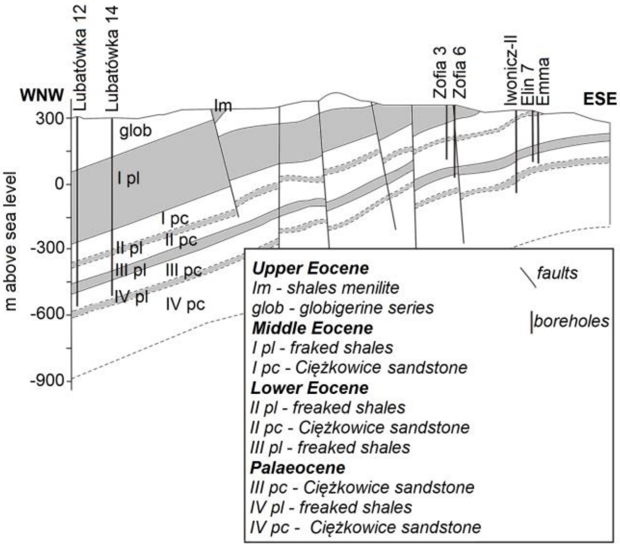

Figure 3. Geological cross section of aquiferus layers of Iwonicz Spa and Lubatówka modified after Kwolek & Skarbek (1995).

## 1.2 Water chemistry of the therapeutic waters

Except for high content of hydrogen sulphide (up to 45 mg.L$^{-1}$) and sulphate ion (112 mg.L$^{-1}$), the chemical composition of the therapeutic water from Róża-III well in Horyniec Spa (Table 1) is rather typical for shallow groundwaters in this area.

Table 1. Archival data on the chemistry (in mg.L$^{-1}$) of the investigated waters, compiled from literature (Porowski, 2001, Duliński et al., 2013) and updated concentrations acquired by the authors during sampling campaign from spa documentations of Horyniec (*), Rymanów (**) and Iwonicz (***).

| **Well (chemical type)** | **TDS** | **HCO$_3^-$** | **Cl$^-$** | **Na$^+$** | **K$^+$** | **Li$^+$** | **NH$_4^+$** | **Ca$^{2+}$** | **Mg$^{2+}$** | **SO$_4^{2-}$** | **F$^-$** | **Fe$^{2+}$** | **Br$^-$** | **B$^-$** | **I$^-$** | **pH** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Róża III*<br>(HCO$_3$-SO$_4$-Mg-Na+H$_2$S)** | 512 | 397 | 15 | 53 | 9.7 | 0.1 | 2.2 | 92.8 | 15.4 | 112.0 | 0.3 | 0.02 | <0.1 | <0.1 | <0.1 | 7.10 |
| **Jaszczew 32 a**<br>(Na-Cl-HCO$_3$+I)** | 15400 | 3306 | 6164 | 5310 | 54.0 | 2.1 | n.m. | 29.0 | 10.0 | 272.0 | 6.9 | 4.50 | 106.0 | 81.9 | 14.2 | 7.83 |
| **Sobniów 29**<br>(Na-Cl-HCO$_3$+I)** | 21148 | 2757 | 10258 | 7588 | 138.0 | 2.7 | n.m. | 40.0 | 9.0 | 154.0 | 7.4 | 0.20 | 66.2 | 67.0 | 16.5 | 7.53 |
| **Moderówka 7**<br>(Na-Cl-HCO$_3$+I)** | 20087 | 3167 | 9369 | 7252 | 30.0 | 1.9 | n.m. | 6.0 | 6.0 | 112.0 | 1.9 | 0.10 | 61.3 | 48.1 | 17.7 | 8.47 |
| **Iskierska 18**<br>(Na-Cl-HCO$_3$+I)** | 27825 | 5123 | 12397 | 9633 | 32.0 | 2.8 | n.m. | 113 | 135.0 | 4.0 | 0.4 | <0.01 | 298.0 | 21.3 | 27.2 | 7.21 |
| **Rudawka 11a**<br>(Na-Cl-HCO$_3$ +I)** | 29650 | 5283 | 13527 | 10487 | 96.9 | 8.4 | n.m. | 65.1 | 30.0 | 8.0 | 0.9 | 13.80 | 39.5 | 27.2 | 13.3 | 7.11 |
| **Iwonicz, well Zofia 6***<br>(Cl-HCO$_3$-Na +Br+ J +B)** | 12500 | 2520 | 5400 | 4220 | 35.9 | 5.2 | n.m. | 71.6 | 27.7 | 4.0 | 0.4 | 0.01 | 18.7 | 42.4 | 3.8 | 6.94 |
| **Iwonicz, well Karol 2***<br>(HCO$_3$-Cl- Na +Fe + F )** | 1570 | 730 | 200 | 390 | 11.1 | 0.6 | n.m. | 54 | 9.6 | 160.0 | 0.1 | 0.28 | 0.53 | 0.4 | 0.1 | 7.49 |
| **Iwonicz, well Iza 19***<br>(HCO$_3$-Cl- Na+ F)** | 765 | 476 | 54 | 143 | 8.0 | 0.4 | n.m. | 48.7 | 10.4 | 13.0 | 0.9 | 0.01 | 0.05 | 2.3 | 0.1 | 7.41 |
| **Iwonicz, well Emma***<br>(Cl-HCO$_3$-Na+I)** | 4370 | 1280 | 1560 | 1380 | 14.0 | 1.0 | n.m. | 52.1 | 14.9 | 2.5 | 1.0 | 1.20 | 8.0 | 25.3 | 1.9 | 7.31 |
| **Iwonicz-II***<br>(Na-Cl-HCO$_3$+I)** | 5518 | 1511 | 2067 | 1808 | 19.7 | 2.5 | 1.7 | 40.1 | 9.9 | 2.0 | 0.2 | 0.01 | 6.2 | 20.3 | 1.5 | 7.68 |
| **Iwonicz, well Elin-7***<br>(Cl-HCO$_3$-Na+I+)** | 5880 | 1590 | 2230 | 1940 | 19.4 | 2.7 | 2.0 | 41.7 | 10.4 | 2.0 | 0.2 | 0.01 | 6.3 | 22.6 | 1.6 | 7.19 |
| **Klimkówka-27***<br>(Cl-HCO$_3$-Na + I,HBO$_2$)** | 12910 | 6170 | 2710 | 3900 | 23.9 | 2.1 | 0.6 | 22.1 | 33.5 | 4.0 | 0.4 | 0.06 | 11.3 | 6.9 | 3.3 | 7.19 |
| **Lubatówka 14***<br>(Cl-HCO$_3$-Na +I)** | 18370 | 3740 | 7990 | 6380 | 36.0 | 4.0 | n.m. | 55.0 | 52.8 | 1.0 | 1.1 | 1.10 | 28.4 | 45.0 | 9.9 | 7.15 |
| **Lubatówka 12***<br>(Cl-HCO$_3$-Na+I)** | 19210 | 3980 | 8300 | 6620 | 40.3 | 3.9 | n.m. | 67.2 | 72.8 | 7.0 | 0.7 | 0.04 | 26.2 | 35.3 | 6.9 | 6.88 |

n.m. = not measured

Sulphur isotope investigations by Żuk et al., (1973) explain the origin of this specific components result of leaching debris of Miocene gypsum, which subsequently is reduced to $H_2S$ by the bacterial activity in presence of organic matter (buried pits).

The majority of the therapeutic waters from Iwonicz Spa and Lubatówka belong to two hydrogeochemical types: Cl–$HCO_3$–Na and $HCO_3$–Cl–Na (Table 1). Total dissolved solids (TDS) in these waters vary from about 1 to over 19 g.$L^{-1}$. Detailed analysis on local hydrochemistry is offered by Dowgiałło (1969), Ciężkowski et al., (1996) and Rajchel et al., (2011). The mineral waters within the Iwonicz anticline belong to the so-called edge oil-field waters or oil-associated waters. They are characterised by high methane content which predominates the gas phase dissolved in the water. This can be seen in all mineral water intakes belonging to Iwonicz Spa and Lubatówka. Moreover, the water from Lubatówka 12 and Lubatówka 14 extracted from depth about 958 m reveal slightly elevated temperature at the outflow (21 °C) and can be considered as thermal (e.g. Porowski 2014). Wells in Lubatówka provide highly mineralized waters for therapy and salt production.

## 2. METHODS

Water samples (Table 2) for noble gas measurements were taken into copper tubes equipped with pinch-off clamps. Samples from the Horyniec and Iwonicz regions were taken from taps used for drinking and other therapeutic purposes. We assumed that both chemical composition of waters and reservoir of dissolved gases remained undisturbed and thus these samples are representative for groundwaters. Nevertheless, a slight modification of their hydrochemical parameters during sampling procedure or within the installations cannot be excluded. Samples from Lubatówka were taken from the tap mounted on the well-head to avoid escape of gas components from water.

Isotope analyses of water samples were performed on a Thermo Finnigan Delta$^{PLUS}$ XP isotope ratio mass spectrometer using a Gas Bench II peripheral unit equipped with a GC-auto sampler. The conventional delta ($\delta$) notation was used and values were reported as permil deviations from the VSMOW standard (Hilkert & Avak, 2004; Mukherjee et al., 2007 and references therein). The internal laboratory standards were calibrated using the normalization procedure described by Nelson (2000). Routine precision better than ±0.2 ‰ and ±2 ‰ was obtained for $\delta^{18}O$ and $\delta^2H$, respectively (Vodila et al., 2011).

Noble gas measurements were performed in the Hertelendy Laboratory of Environmental Studies, Debrecen, Hungary. First, the dissolved gases from the water samples were removed and then the noble gas content was measured using VG5400 mass spectrometer. The reproducibility of noble gas measurements for samples of 20-40 ml allows us to determine the solubility temperatures with the uncertainty of around 0.5°C (Papp et al., 2012). Noble gas temperatures were calculated by means of the Noblebook excel sheet of Aeschbach-Hertig (Aeschbach-Hertig et al., 2000).

Tritium concentration in water was determined using the $^3He$ ingrowth method. The measurement technique has a detection limit of 0.012 TU, and the precision is 2.4% between 1 and 20 TU (Palcsu et al., 2010).

The $^{14}C$ content of dissolved inorganic carbonate (DIC) in Róża-III spring water was measured by accelerator mass spectrometry using a MICADAS type AMS in the Hertelendi Laboratory (Molnár et al., 2013a). During sample preparation 20 ml of water was reacted with phosphoric acid in a vacuum reaction cell. A necessary amount (> 2 mg) of the obtained $CO_2$ was measured by $^{14}C$ AMS (Molnár et al., 2013b). Standard deviation of radiocarbon measurements of dissolved inorganic carbon from groundwater samples was equal to ±0.5 pMC.

## 3. RESULTS AND DISCUSSION

### 3.1. Horyniec Spa

The sample of Róża-III was taken for analysis from the study site of Horyniec Spa. This water has moderate ionic composition dominated by sodium, calcium and sulphate ions (Table 1). The $\delta^{18}O$ and $\delta^2H$ values are -10.3‰ and -71‰, respectively, indicating the meteoric origin of water (Fig. 4). To estimate the age of water $^{14}C$ analysis has been used.

The $^{14}C$ activity of dissolved inorganic carbon (DIC) in water from the Róża III borehole equals to 25.55 pMC. Using a standard formula with Pearson correction the age of water can be estimated at the level of about 6000 years. This confirms the earlier estimation calculated by Ciężkowski et al., (2003).

The elevated helium concentration ($3.72 \cdot 10^{-7}$ ccSTP/g) corresponds to the age of the water (Table 3). The low $^3He/^4He$ isotope ratio ($R/R_a$=0.21, where R and $R_a$ are $^3He/^4He$ isotope ratios in water and in atmosphere; $R_a = 1.384 \cdot 10^{-6}$) indicates crustal origin of helium in groundwater. The water is enriched in $^4He$ due to alpha-particle emitting isotopes of the uranium and thorium decay chains.

Table 2. The geographical parameters of the therapeutic water wells

| Well | Latitude | Longitude | Surface elevation [m a.s.l.] | Depth (m) | Geological formation | Initial depth of borehole (m) |
|---|---|---|---|---|---|---|
| Horyniec, well Róża III | 50°11' N | 23°21' E | 260.0 | 29.0–30.5 | Miocene sandstone | 29.0 |
| Iwonicz, well Iwonicz-II | 49°56' N | 21°71' E | 451.35 | 366.3 - 394.8 | Ciężkowice Sandstone II and III | 394.8 |
| Iwonicz, well Elin-7 | 49°56' N | 21°78' E | 431.8 | 85.0-238.0 | Ciężkowice sandstone II | 1030.0 |
| Klimkówka, well Klimkówka -27 | 49°33' N | 21°47' E | 462.78 | 417.0-481.0 | Ciężkowice sandstone III | 1255.0 |
| Lubatówka, well Lubatówka-14 | 49°55' N | 21°76' E | 351.0 | 568.0-662.0<br>and<br>688.0-816.0 | Ciężkowice sandstone II and IV | 820.0 |
| Lubatówka, well Lubatówka-12 | 49°55' N | 21°74' E | 350.74 | 625.0-728.0<br>756.0-840.0<br>881.0-958.0 | Ciężkowice sandstone I, II and III | 1151.5 |

Table 3. Noble gas concentrations, helium isotope ratios and calculated noble gas temperatures of the therapeutic waters in SE Poland.

|  | $He\cdot10^8$ | $Ne\cdot10^7$ | $Ar\cdot10^4$ | $Kr\cdot10^8$ | $Xe\cdot10^9$ | $R/R_a$ | NGT (°C) | Remarks |
|---|---|---|---|---|---|---|---|---|
|  | ccSTP/g |  |  |  |  |  |  |  |
| Horyniec, well Róża III | 37.2 | 2.79 | 4.55 | 10.34 | 14.6 | 0.210 | 7.6* | CE |
| Iwonicz, well Iwonicz-II | 4.6 | 0.14 | 2.42 | 6.63 | 10.3 | 0.978 | 13.0** | SD, contains $CH_4$ |
| Iwonicz, well. Elin-7 | 5.0 | 0.96 | 2.38 | 6.10 | 9.7 | 0.961 | 14.4** | SD, contains $CH_4$ |
| Klimkówka, well Klimkówka-27 | 5.7 | 1.29 | 2.84 | 6.68 | 9.2 | 0.470 | 18.4** | DD, contains $CH_4$ |
| Lubatówka, well Lubatówka-12 | 604.6 | <0.01 | <0.02 | <0.01 | <0.01 | 0.012 | - | High $CH_4$ content |
| Lubatówka, well Lubatówka-14 | 104.9 | <0.01 | <0.02 | <0.01 | <0.01 | 0.014 | - | High $CH_4$ content |
| AEW (995 hPa, 7.6 °C) | 4.62 | 2.03 | 4.01 | 9.59 | 14.09 | 0.983 |  |  |

ccSTP: cubic centimetre at standard temperature (0°C) and pressure (1013.25 hPa)
AEW: air equilibrated water
$R/R_a$: $^3He/^4He$ isotope ratios in the water (R) and atmosphere ($R_a$)
pMC: percent modern carbon
NGT: noble gas temperature
CE: closed-system equilibration model; SD: solubility driven equilibration model; DD: diffusive degassing model
*: 1σ uncertainty of NGT determination is 0.6 °C; **: 1σ uncertainty of NGT determination is more than 2.5 °C

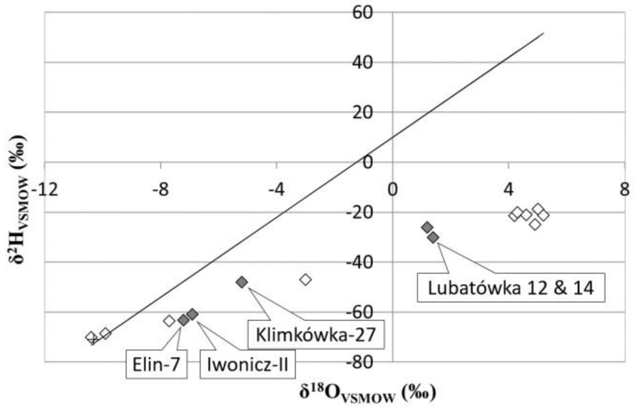

Figure 4. Stable isotope compositions of groundwaters in the Iwonicz region. Filled diamond represents data of this study, open diamond marks data from Porowski (2006), the straight line represents the global meteoric water line (GMWL). A cross representing isotope data for Róża-III from Horyniec Spa was added.

Measured concentrations of dissolved atmospheric noble gases allow the determination of recharge temperatures by using different gas partitioning models (Aeschbach-Hertig et al., 2008). The noble gas concentrations and the calculated noble gas solubility temperatures of groundwater samples are shown in Table 3. Aside helium, the water sample taken from Róża III borehole has similar noble gas concentrations as water samples that are equilibrated with the atmosphere, indicating a closed system behaviour. Therefore, he closed-system equilibration model (Aeschbach-Hertig et al., 1999) was applied in order to calculate a reliable noble gas recharge temperature for Róża III. These suggest that air temperature was 7.6±0.6°C at the time of infiltration.

Today mean annual air temperature in SE Poland is ~8°C and the long term Holocene temperature oscillation is reported to be up to 1°C (Korhola et al., 2002). Therefore, the obtained noble gas temperature of 7.6ºC remains in good agreement with the mean air temperature of the Horyniec region during the Holocene.

### 3.2 Iwonicz Spa and Lubatówka

Prevailing chemical components mainly sodium and chloride of Iwonicz waters (Iwonicz-II, Elin-7 and Klimkówka-27) seems to be influenced by mineral waters of the Lubatówka aquifer, the latter located in a 10-20 m thick Palaeocene freaked shale layer at 900 m depth. Water of the Iwonicz aquifer is stored in the Palaeocene Ciężkowice Sandstone at 300-400 m depth that is located between two freaked shale layers (Fig. 3) As the study area is moved by faults, water bodies of the different sedimentary layers might communicate with each other. For this reason, chemical compositions of Iwonicz and Lubatówka waters may be related to each other.

Stable isotope analyses (Table 4) indicate an enrichment in heavy isotopes, typical for mixing of modern infiltration and deep formation waters. This latter water body was entrapped during the formation of the sedimentary environment. The water was a part of the ancient Paratethys ocean, which became enriched in heavy isotopes of hydrogen and oxygen ($^{2}$H, $^{18}$O) during its evaporation. As sediment was deposited in the shelf areas and/or basins, this isotopically heavy water was entrapped (Bozau et al., 2015). Our results are consistent with previous findings (Porowski, 2006; Baran & Hałas, 2011) suggesting that Lubatówka waters are the mixture of three types of water: meteoric water, formation water (connate water) and dehydration water.

These authors argued that the increase of total dissolved solids and Cl- concentration together with the observed, highly positive values of $\delta^{18}$O, $\delta^{2}$H and the depth of the water bodies support the idea of mixed origin. However, the contribution of meteoric water is low compared to relict, formation waters (Porowski, 2006; Baran & Hałas, 2011). The $\delta^{2}$H and $\delta^{18}$O values of most samples are out of the GMWL and form a straight line suggesting mixing of a two-component system consisted of meteoric and formation waters. The mixing proportions of these components in the Iwonicz Spa depend on the definition of stable isotope composition of the formation water end member.

Assuming water from Lubatówka to be representative for the deep formation component its contribution in Iwonicz II, Elin-7 and Klimkówka 27 boreholes can be estimated at the level of 25%, 21%, and 49%, respectively. This contribution becomes slightly lower (19%, 16% and 38%, respectively) when waters from Jaszczów, Moderówka, Iskierska and Rudawka are considered to be characteristic of the pure formation component, as the end member of the mixing. Regardless of the assumed stable isotope composition of the formation water, mineral waters of the discussed area are evidently dominated by meteoric waters. This is supported by results of earlier investigations (Ciężkowski et al., 1996, Duliński et al., 2013).

Noble gas concentration studies provide a tool for determining the contribution of different water components in a given water body. Waters from Lubatówka are highly enriched in helium ($1\text{-}6\cdot10^{-6}$ ccSTP/g). Their concentration is 25-150 times higher than that measured in surface water. Detected low R/R$_a$ ratios (0.012 and 0.014) indicate that $^{4}$He is of radiogenic origin in these waters.

Table 4. Stable isotope composition of mineral waters in Horyniec and the Iwonicz region.

| | $\delta^{18}O_{VSMOW}$ [‰] | $\delta^{2}H_{VSMOW}$ [‰] | Remarks |
|---|---|---|---|
| Horyniec Róża-III | -10.3 | -71 | This study |
| Jaszczew 32a | 4.9 | -25 | Porowski (2006) |
| Sobniow 29 | 5.2 | -21 | |
| Moderówka 7 | 4.6 | -21 | |
| Iskierska 18 | 4.2 | -21 | |
| Rudawka 11a | 4.3 | -20 | |
| Zofia 6 | -3.0 | -47 | |
| Karol 2 | -9.9 | -68 | |
| Iza 19 | -10.4 | -70 | |
| Emma | -7.7 | -63 | |
| Iwonicz-II | -6.9 | -61 | This study |
| Elin-7 | -7.2 | -63 | |
| Klimkówka 27 | -5.2 | -48 | |
| Lubatówka 14 | 1.4 | -30 | |
| Lubatówka 12 | 1.2 | -26 | |

The other noble gases, including neon, argon, krypton and xenon remained undetectable in these samples. These noble gases are absent since they have been washed-out when the water body was in contact with a relatively large reservoir of methane and carbon dioxide. The absence of the heavier (from neon to xenon) dissolved gasses suggests that outgassing has happened since their concentrations are lower than that of air equilibrated (AEW) surface water. This idea of methanogenesis followed by methane oxidation is further confirmed by high $\delta^{13}C$ values of DIC, within the range between +19.9 and +24.0‰ vs. VPDB (Baran & Hałas, 2011).

Iwonicz-II, Klimkówka-27 and Elin-7 waters are characterised by low helium concentrations, close to equilibrium values with the bulk atmosphere (Table 3). The $R/R_a$ (0.96-0.98) ratio found in waters of Iwonicz-II and Elin-7 is close to the atmospheric value, while water from Klimkówka-27 borehole contains small amount of radiogenic He, which is further confirmed by its $R/R_a$ ratio (0.47). However, all these samples either have suffered subsurface degassing or are mixtures of waters with low noble gas contents. Table 3 shows that some noble gases are absent in waters of Lubatówka. As it was mentioned above, the lack of heavier noble gases (Ne to Xe) can be explained by mixing with a substantially high salinity end-member of very low noble gas concentrations (expect for He) due to degassing to a huge methane gas phase. Using two degassing models (Table 3) we could calculate recharge temperatures (13.0ºC, 14.4ºC and 18.4ºC), but these temperatures have to be handled with care. These noble gas recharge temperatures indicate that the waters do have a component which can be considered as freshly recharging meteoric water. Nevertheless, as the other component with low noble gas concentrations has lowered the noble gas amounts in the waters, it causes a shift towards higher recharge temperatures.

One of the main goals of this study was to establish the mean residence time of the meteoric component using tritium and noble gases concentrations, including the tritium daughter - $^{3}He$. If tritiogenic $^{3}He$ dissolved in water samples had been detected, then a $^{3}H/^{3}He$ age could be calculated. The water samples from the Iwonicz region taken in the autumn in 2012 contained tritium indicating the presence of fresh component. In Fig. 5 are shown the changes of tritium concentration in waters from Iwonicz over the last two decades. In each case, tritium concentrations were continuously decreasing in time. In September 2012, the highest tritium content was found in Elin-7 borehole (2.38±0.69 TU), while in water from Klimkówka-27 tritium was close to detection limit (0.069±0.015 TU). The tritium concentration in Iwonicz-II water was 1.53±0.05 TU. The decreasing trend was parallel to the tritium time series available for precipitation in Kraków and the same with Eastern Hungary.

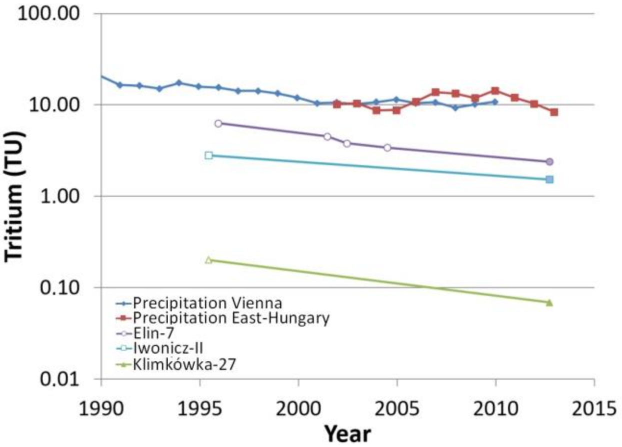

Figure 5. Comparison of tritium concentrations of Iwonicz waters with the levels observed in precipitation (samples taken in September 2012 belong to this study, previous results are from Porowski, 2001, and Duliński et al., 2013. Precipitation data for Kraków precipitation from was provided by the GNIP database, while values for precipitation from Hungary were collected and measured by the first author of this study).

It is unlikely that lower tritium concentrations in our waters are due to changes in the mixing proportion between the fresh water and old tritium-free formation water over the last decades. Therefore we conclude that rather the initial tritium concentration in fresh water component is decreasing as in the precipitation, although we may not neglect the influence of aquifer geometry and its matrix porosity. Significant tritiogenic $^{3}He$ cannot be detected, since the $^{3}He/^{4}He$ ratios (Table 1) are close to or lower than the atmospheric isotope ratio. The fresh water component must have a noble gas pattern close to equilibrium with the atmosphere, while the formation component is assumed to have a noble gas composition of Lubatówka samples with high helium and extremely low heavier noble gas contents.

Concentrations of heavy noble gases in water samples from the Iwonicz Spa are below the equilibrium values with the atmosphere. This could be explained by the presence of a noble gas free (Ne-Xe) old component, but the helium concentrations are too low $(4.6\text{-}5.7)\cdot 10^{-8}$ ccSTP/g. Other processes such as a third component of the water, as proposed by Duliński et al. (2013), or further degassing and/or re-equilibration with the atmosphere may be assumed. These processes might reset the helium component down to the equilibrium value and $^{3}He/^{4}He$ close to the atmospheric isotope ratio. These effects might eliminate the tritiogenic $^3$He component. In this case, the residence time of the fresh component might be even 1-2 decades, since the low tritium content does not allow higher age when taking the mixing ratios of the meteoric component obtained from the stable isotope signature into account. Unfortunately, as we know very little about the residence time of the meteoric component, we can only constrain it between 0 and 2 decades. If these waters do not have a larger tritiogenic $^3$He contribution, the age of the fresh component might be just a few years. However, a pure binary mixing of recently infiltrated meteoric water with formation water should be excluded.

## 4. CONCLUSIONS

Groundwater from the well Róża-III is of purely meteoric origin, and seems to have infiltrated in the middle Holocene as indicated by its $^{14}$C content equal 25.55 pMC. Noble gas concentrations in the Horyniec region do not show subsurface degassing, therefore a reliable noble gas recharge temperature could be calculated by applying the closed-system equilibration model. The recharge temperature has been estimated to be 7.6°C, which corresponds to the mean air temperature of the Horyniec region during the Holocene.

Therapeutic waters in the Iwonicz region show a different pattern. Lubatówka waters are enriched in helium and do not contain any other atmospheric noble gases. This latter is either due to subsurface degassing forced by the presence of a large reservoir of methane being in contact with ground waters, or by formation origin of these waters. The stable isotope signature of Lubatówka and Iwonicz waters implies a high contribution of formation water enriched in heavy isotopes of oxygen and hydrogen. Iwonicz waters, and maybe to some extent Lubatówka waters are mixtures of meteoric water and old, formation water with very low noble gas content, although presence of a third component cannot be excluded. The mean residence time of the freshwater component in therapeutic water has been calculated to be up to 1-2 decades.

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### REFERENCES

**Aeschbach-Hertig W., Peeters F., Beyerie U. & Kipfer R.,** 1999. *Interpretation of dissolved atmospheric noble gases in natural waters,* Water Resources Research, 35: 2779-2792.

**Aeschbach-Hertig W., El-Gamal H., Wieser M. & Palcsu L.,** 2008. *Modeling excess air and degassing in groundwater by equilibrium partitioning with a gas phase,*Water Resources Research, 44: 449-461.

**Aeschbach-Hertig, W., Peeters F., Beyerle U. & Kipfer R..** 2000. *Palaeotemperature reconstruction from noble gases in groundwater taking into account equilibration with entrapped air.* Nature, 405:1040-1044.

**Baran A. & Hałas S.,** 2010. *Isotope study of therapeutic waters from Horyniec Spa, SE Poland,* Isotopes in Environmental and Health Studies, 46: 454-462.

**Baran A. & Hałas S.,** 2011. *Isotopic investigation of mineral waters of Iwonicz-Zdrój and Lubatówka* (in Polish), Biuletyn Państwowego Instytutu Geologicznego, 444: 5–14.

**Bozau E., Sattler C.D., & Berk W.,** 2015. *Hydrogeochemical classification of deep formation waters,* Applied Geochemistry, **52**: 23–30.

**Cwanek J., Kędzierski A., Kuzora W., Kwaśnicki K., Linkowski R., Loose- Kuzora M., Lubaś J., Michalak J., Papierkowski J., Papierkowski S., Piątkowski S., Rajchel J., Ross J., Walter - Croneck K. & Wróblewski Z.,** 1985. *Iwonicz Zdrój. Monografia* (in Polish), Przedsiębiorstwo Państwowe „Uzdrowisko Iwonicz", 2nd edition, Kraków.

**Ciężkowski W., Kabat T., Liber-Madziarz E., Przylibski T., Teisseyre B., Wiśniewska M. & Zuber A.,** 1996. Określenie obszarów zasilania wódleczniczych pochodzenia infiltracyjnego w Polsce na podstawie badań izotopowych*, Zakład Badawczo-Usługowy „Zdroje",*Wrocław, 10: 6-12.

**Ciężkowski W., Porwisz B. & Zuber A.,** 2003. *The origin and age of $H_2S$-bearing waters in Horyniec Spa and Latoszyn,* In: Kozierski, B. and Jaworska-Szulc B. (Editors) Contemporary Problems in Hydrogeology (in Polish), 11, 2: 95-102, PG Gdańsk.

**Dowgiałło, J.,** 1969. *Occurrence of therapeutic waters in Poland, Geology of balneological resources* (in Polish). In: Dowgiałło, J., Karski, A. and Potocki, L., (Editors): 143-211. Geological Publishing House, Warsaw.

**Duliński M., Rajchel L., Czop M., Motyka J. & Rajchel J.,** 2013. *Isotope inwestigations of mineral waters in the Iwonicz-Rymanów area (East Carpathians, Poland),* Biuletyn Państwowego Instytutu Geologicznego, 456: 127-132.

**Hilkert A.W. & Avak H.**, 2004. Finnigan Gas Bench II: $^{18}$O-Equilibration on Water, Fruit Juice and Wine, Application Note: 30048.

**Korhola A., Vasko K., Toivonen H.T.T. & Olander H.,** 2002. Holocene temperature changes in northern Fennoscandia reconstructed from chironomids using Bayesian modelling, Quternary Science Reviews, 21: 1841-1860.

**Kwolek S. & Skarbek K.,** 1995. *Dokumentacja geologiczna złoża ropy naftowej antykliny Iwonicza*

*Zdroju (Iwonicz Zdrój, Zboiska, Draganowa),* in: Kamiński J. and Mackoś W. (eds.) Budowa geologiczna Iwonicza Zdroju i okolic, Wyd. Iwonicz Zdrój.

**Meszczyński, J. & Dziewa K.,** 2002. Explainations to Hydrogeological Map of Poland, In: 50, 000 Scale, the HoryniecSheet 960 (in Polish), Works State Geol. Inst., Warsaw.

**Molnár M., Rinyu L., Veres M., Seiler M., Wacker L. & Synal H-A** (2013a). *EnvironMICADAS: a mini $^{14}C$ AMS with enhanced Gas Ion Source Interface in the Hertelendi Laboratory of Environmental Studies (HEKAL), Hungary.* Radiocarbon, 55: 338–344.

**Molnár M., Janovics R., Major I., Orsovszki J., Gönczi R., Veres M., Leonard AG., Castle SM., Lange TE., Wacker L., Hajdas I. & Jull AJT** (2013b). Status report of the new AMS $^{14}$C sample preparation lab of the Hertelendi Laboratory of Environmental Studies (Debrecen, Hungary) Radiocarbon, 55: 665–676.

**Mukherjee, A., Fyrar, A.E. & Rowe, H.D.,** 2007. *Regional-scale stable isotopic signatures of recharge and deep groundwater in the arsenic affected areas of West Bengal, India,* Journal of Hydrology, 344: 151–161.

**Nelson, S.T.,** 2000. *A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analysed by continuous flow methods,* Rapid Communication in Mass Spectrometry, 14: 1044–1046.

**Oszczypko, N.,** 1981. *Impact of the Neogene restructuring of the Carpathian foreland on hydrodynamic and hydrochemical conditions of the Carpathian foreland sink,* Bulletin of the Geological Institute, 325: 5-87.

**Oszczypko, N.,** 1999. *Course of the Miocene subsidence in Polish part of the Carpathian foreland sink,* Works of the State Geological Institute, 168: 209-230.

**Paczyński, B. & Sadurski,** A. (eds.), 2007. *Regional hydrogeology of Poland vol. II, Mineral, therapeutic, thermal as well as mine waters,* State Geological Institute, Warsaw.

**Palcsu L., Major Z., Köllő Z. and Papp L.**, 2010. *Using an ultrapure $^4$He spike in tritium measurements of environmental water samples by the $^3$He-ingrowth method,* Rapid Communications in Mass Spectrometry, 24: 698-704.

**Papp L., Palcsu L., Major Z., Rinyu L. & Tóth I.,** 2012. *A mass spectrometric line for tritium analysis of water and noble gas measurements from different water amounts in the range of microlitres and millilitres,* Isotopes in Environmental and Health Studies,**48** (1): 494-511.

**Poprawa D. & Nemcok J.,** (eds) 1989. Geological atlas of Western Outer Carpathians and their foreland, State Geol. Institute, Warsaw.

**Porowski A.,** 2001. *Chemical composition and origin of ionic ratios in the Iwonicz anticline mineralized groundwaters (Polish outer Carpathians),* Ann. Soc. Geol. Pol., 71: 125-134.

**Porowski A.,** 2006. *Origin of mineralized waters in the central Carpathian Synclinorium, SE Poland,* Stud. Geol. Pol., 125: 5-67.

**Porowski A.,** 2014. Chemical and isotopic characteristics of thermal waters in the Carpathian region: Implications to the origin and resources, in: Balderer W., Porowski A., Idris H., LaMoreaux J.W. (Editors) *Thermal and mineral Waters, Origin, properties and Applications,* Springer_Verlag, Berlin.

**Rajchel L., Czop M., Motyka J. & Rajchel J.,** 2011. *Chemistry of the mineral and therapeutic water from Iwonicz–Rymanów region,* Bulletin of the Geological Institute, 445: 549-560.

**Vodila G., Palcsu L., Futó I. & Szántó Z.** 2011. *A 9-year record of stable isotope ratios of precipitation in Eastern Hungary: Implications on isotope hydrology and regional palaeoclimatology,* Journal of Hydrology, 400: 144-153.

**Wdowiarz S.,** 1985. *On geological structure and oil- and gas baring rocks of Central Carpathian Synclinoriumin, Poland* (in Polish), 350: 5-49.

**Żuk, W., Szaran, J., Hałas, S. & Lis, J.,** 1973. *Results of the isotopic composition of sulphur in mineral springs within the territory of Poland* (in Polish), Przegląd Geol.,5: 271-273.

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