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Noble gas constraints on genesis of therapeutic waters from SE Poland

Laszlo PALCSU[1], Anna BARAN[2], Ireneusz BARAN[2], Stanisław HAŁAS[3]

[1]*Institute of Nuclear Research, H-4026 Debrecen, Bem tér 18/c, Hungary; e-mail: palcsu@atomki.hu*
[2]*Institute of Technical Engineering, Bronisław Markiewicz State School of Higher Vocational Education in Jarosław, 16 Czarnieckiego St., 37-500 Jarosław, Poland; e-mail: annabaran1212@o2.pl*
[3]*Spectrometry Mass Laboratory, Institute of Physics, Maria Curie-Skłodowska University, 1 Maria Curie-Skłodowska Sq., 20-031 Lublin; e-mail: stanisław.halas@umcs.pl*

The territory of southeastern Poland, but especially its southern part, is rich in various mineral and therapeutic waters of high quality. The balneological resources of the region and in particular its mineral and therapeutic waters of Iwonicz Spa, Lubatówka and Horyniec Spa are exceptional. The previous studies (Baran, Hałas 2010, 2011) have shown that these waters are mixtures of recently recharging water, ascending salty dehydration water and brine from oil fields. Five groundwater samples have so far been analyzed for noble gas concentration and isotope ratios. The results obtained are summarized in Table 1.

Table 1. Noble gas concentrations, helium isotope ratios and calculated noble gas temperatures of the therapeutic waters in southeastern Poland

Locality	$He \cdot 10^8$	$Ne \cdot 10^7$	$Ar \cdot 10^4$	$Kr \cdot 10^8$	$Xe \cdot 10^9$	R/R_a	^{14}C (pMC)	NGT (ºC)	Remarks
	ccSTP/g								
Horyniec R.-III	37.2	2.79	4.55	10.34	14.6	0.210	25.55	7.6	CE
Lubatówka-12	604.6	<0.01	<0.02	<0.01	<0.01	0.012	n.a.	-	Lot of gas (CH_4)
Lubatówka-14	104.9	<0.01	<0.02	<0.01	<0.01	0.014	n.a.	-	Lot of gas (CH_4)
Iwonicz-II	4.6	0.14	2.42	6.63	10.3	0.978	n.a.	13.0	SD, contains CH_4
Klimkówka-27	5.7	1.29	2.84	6.68	9.2	0.470	n.a.	18.4	DD, contains CH_4
AEW (995 hPa, 0ºC)	4.6	2.03	4.01	9.59	14.10	0.983			

ccSTP: cubic centimetre at standard pressure and temperature (1013.25 hPa, 0ºC)
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
n.a.: not analyzed

Based on the chemical and isotopic analyses of noble gases, three genetic groups of therapeutic waters can be distinguished:

1. Lubatówka waters are enriched in helium. They are mainly of crustal origin, which is evidenced by the isotope ratios (R/R_a represents the $^3He/^4He$ isotope ratio (R) compared to the atmospheric isotope ratio (R_a)). These low R/R_a ratios (0.012 and 0.014) show that radiogenic ^4He prevails in these waters. It is in good agreement with

the previous findings. The Lubatówka water can be assigned to typical brines from oil fields. This water contains methane which has light carbon isotopic composition, whilst carbon isotope ratio of bicarbonate attained extremely heavy $\delta^{13}C_{PDB}$ values (+19.9 to +24.0‰) as a result of isotope fractionation. Moreover, the other noble gases, namely neon, argon, krypton and xenon were not detected in the Lubatówka samples. The explanation of this pattern is that the water is in a contact with a huge gas phase composed mainly of methane, and the atmospheric noble gases could escape from the water to the gas phase. Additionally, methane gas bubbling through the brine aquifer was able to carry away the originally dissolved gases from the water. On the other hand, if these waters were of dehydration origin, as can be seen from the stable isotopic composition of water ($\delta^{18}O_{SMOW}$: +1.25‰, $\delta^{2}H_{SMOW}$: -31‰), the concentrations of noble gases (except for helium) would have to be substantially low.

2. Iwonicz-II and Klimkówka-27 waters contain relatively low concentrations of He, close to the solubility equilibrium. Klimkówka-27 waters contain a small amount of radiogenic He, which is evidenced by the R/R_a value (0.47). The R/R_a (0.978) of Iwonicz-II waters is close to the atmospheric ratio. However, these samples have suffered subsurface degassing. It can be seen from Ne-Ar-Kr-Xe concentrations that some noble gases are missing. We are aware from the previous studies that these waters are mixtures of freshly recharging waters similar to those of Lubatówka. The lack of heavier noble gases can be explained by dilution of noble gas concentrations in the methane-rich waters. Using two degassing models (Aeschbach-Hertig et al. 2008), we could calculate recharge temperatures (13.0ºC and 18.4ºC, respectively), but these temperatures have to be handled with care.
3. Róża-III seems to be groundwater that infiltrated the surface in the middle Holocene (^{14}C content: 25.55 pMC). Noble gas concentrations do not show subsurface degassing, therefore a reliable noble gas recharge temperature could be calculated using the closed-system equilibration model. The recharge temperature obtained is 7.6 ºC, which is in good agreement of the mean air temperature of the Horyniec region during the Holocene.

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