ASSESSING THE POTENTIAL OF TRIPLE ISOTOPE ANALYSES OF WATER (δ^2H, $\delta^{18}O$, $\delta^{17}O$) IN GROUNDWATER HYDROLOGY: EXAMPLES FROM POLAND

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INTRODUCTION

Two case studies illustrating potential of triple isotope analyses of water (δ^2H, $\delta^{18}O$, $\delta^{17}O$) in groundwater hydrology are presented here:



- **Quantification of interaction between recent infiltration waters and diagenetic waters in the Wysowa Spa region, Southern Poland. The mineral waters of the Wysowa Spa region are mixed waters containing two major components in varying proportions: (i) highly mineralized diagenetic water of deep circulation, reaching the surface through system of fissures and faults, and (ii) local infiltration water.**

- **Assessment of the origin of heavy brines in the Klodawa Salt Mine, Central Poland. The Klodawa salt deposit is situated in the central part of a 63 km long salt structure. That part pierces through the Mesosoic strata and forms a diaphir 26 km long and 0.5-2 km wide. Salt is exploited at four main levels: 450, 525, 600 and 750 m and several intermediate levels. The volume of exploitation chambers is approximately 18 millions of cubic meters, with typical dimensions 120 x 12 x 12 m. Three shafts are operated. The mine is producing approximately 6×10^5 tons of salts annually. Isotope analyses of water appearances in Polish salt mines started in early the 1970s [1-2]. Soon it became clear that analyses of oxygen and hydrogen stable isotope composition of water constitute a powerful tool for determination the origin of mine waters, thus helping to assess the risk associated with uncontrolled water inflows.**

METHODS

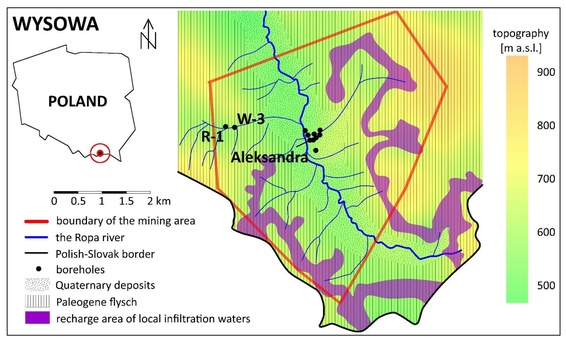
WYSOWA	KLODAWA
CRDS laser spectroscopy (Picarro L2140-*i*) [3]	
Direct analysis of δ^2H, $\delta^{18}O$, $\delta^{17}O$	High-temperature distillation Analysis of δ^2H, $\delta^{18}O$, $\delta^{17}O$
Electrolytic Enrichment & Liquid Scintillation Spectrometry	**Isotope-Ratio Mass Spectrometry (Finnigan Delta S)**
Tritium concentration	High-temperature distillation δ^2H: Zn reduction + IRMS $\delta^{18}O$: CO_2-water equilibration+IRMS
3. ICP-MS	
Chemical composition	



RESULTS

WYSOWA SPA

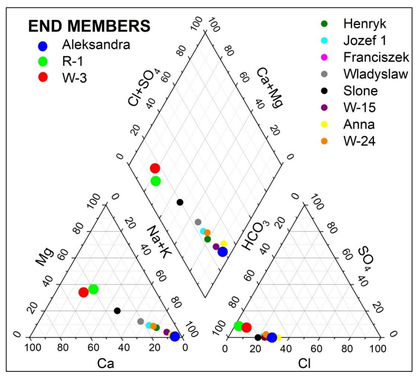
The Wysowa Spa is located in southern Poland, in the upper reaches of Ropa river draining part of the Beskid Niski mountain range. The catchment of Ropa river is underlain by Paleogene-Cretaceous flysch formations covered by Quaternary deposits. Mineral and therapeutic CO_2-rich waters occur in the central part of Wysowa Spa. They are exploited from depth interval of ca. 15 to 100 m by eleven wells distributed over the area of ca. 0.28 km^2.The exploited mineral waters are mixed waters containing two major components in varying proportions. One end-member, represented by water originating from Aleksandra well, is a highly mineralized diagenetic water of deep circulation, reaching the surface through system of fissures and faults. The second end-member is represented by local infiltration water, either recent one, or aged of pre-bomb (Holocene) age.



Water chemistry

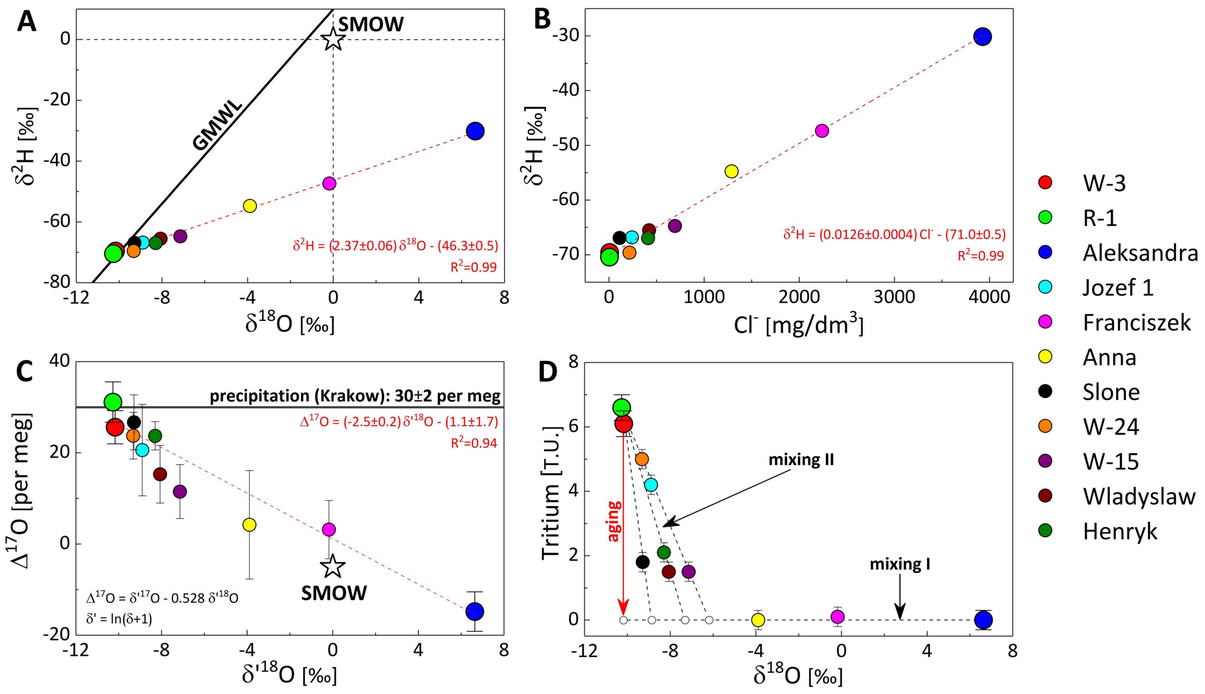
Mineral waters of Wysowa Spa are HCO_3-Cl-Na, HCO_3-Na and HCO_3-Na-Ca waters containing trace constituents with specific pharmacological activity, such as bromine, iodine, iron and metaboric acid. The TDS range from 2.3 g/dm^3 in Jozef I well to 23.4 g/dm^3 in the Alexandera well.

The dominance of HCO_3 ion, as well as variability of the chemical composition of Wysowa waters, are clearly visible in the Piper diagram. Water from Aleksandra well is enriched in Cl^- and Na^+ ions and contains geogenic carbon dioxide. In wells W-3 and R-1, representing recent infiltration water, the concentration of Cl^- and Na^+ ions decreases in favor of Ca^{2+} ions.



Mixing patterns

Isotope and chemical data, when plotted in different space coordinates (δ^2H-$\delta^{18}O$, δ^2H-Cl^-, $\Delta^{17}O$-$\delta'^{18}O$, ^3H content vs $\delta^{18}O$), suggest strong interaction between local infiltration waters and the diagenetic water represented by the Aleksandra well.



Closer examination of Fig. D above reveals that the data points on ^3H-$\delta^{18}O$ plot form in fact two mixing lines. The Aleksandra diagenetic end-member mixes with infiltration water of pre-bomb (Holocene) age which is devoid of tritium and has ^{18}O isotope signature of recent recharge (ca. -10.2‰, average of W-3 and R-1 wells). Anna and Franciszek wells follow this mixing line (Mixing I). They reveal intermediate $\delta^{18}O$ values and are devoid of tritium. The remaining wells plot on the second mixing line(s) (Mixing II) connecting the recent infiltration end-member represented by W-3 and R-1 water, characterized by high tritium content, with the end-member devoid of tritium and having $\delta^{18}O$ signature defined by the cross point of the two mixing lines (cf. Fig. D). Those two mixing systems are separated in space, as suggested by differences in depths of the investigated groups of wells. The above-outlined mixing patterns are consistent with the data shown on the remaining plots (Figs. A,B,C above).

The position of Aleksandra end-member on the δ^2H-$\delta^{18}O$ plot (cf. Fig A) may result from several processes: iii) possible isotope effects accompanying ultrafiltration processes which presence was postulated for the Carpathian flysh [4], (ii) isotope re-equilibration between structural water and clay minerals at temperatures characterizing diagenesis of the Carpathian flysh, (150-200^{o}C), or (iii) possible isotope effects occurring during compaction and release of structural water in the course of diagenesis. However, negative $\Delta^{17}O$ value of the diagenetic end-member (ca. -15 per meg) may also indicate evaporative marine environment in which clay minerals present in the Carpatian flysh were formed.

KLODAWA SALT MINE





Three main groups of waters

Syngenetic brines

- **Waters representing different stages of the evolution of Zechstein sea during desiccation of shallow lagoons**
- **Brines closed within salt pockets usually appear in the mine in limited quantities**

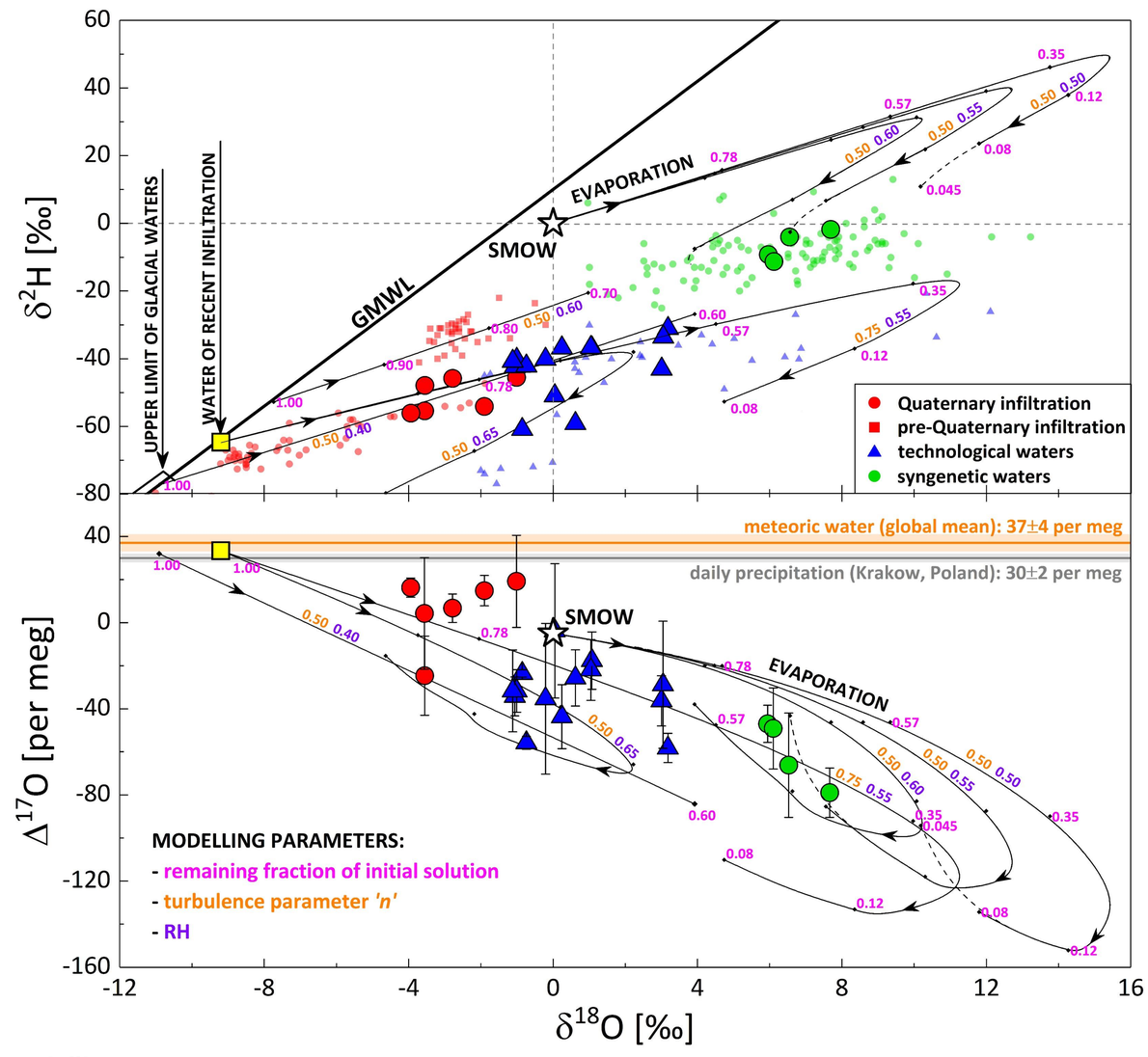
Paleowaters

- **Paleoinfiltration waters of different age (Quaternary/Pre-Quaternary)**
- **Most of them carry significant evaporation signatures**

Technological waters

- **Local meteoric waters used inside the mine for various purposes, usually heavily enriched due to evaporation in dry atmosphere of the mine**

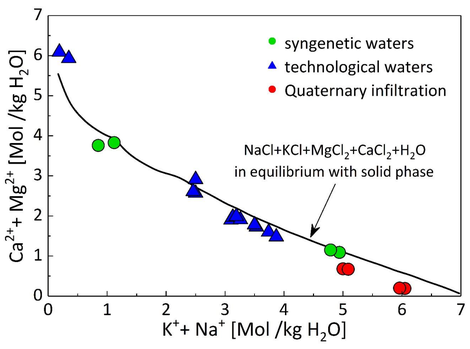
Those three groups of waters are characterized by different $\Delta^{17}O$ values, pointing to differences in their evaporation histories; highest $\Delta^{17}O$ values are observed for waters of meteoric origin (ca.+20 per meg) whereas lowest $\Delta^{17}O$ values (up to -80 per meg) were measured in syngenetic brines.



Modelling:

I. Isotope and chemical evolution of sea water undergoing evaporation was modelled in the δ^2H-$\delta^{18}O$ and $\Delta^{17}O$-$\delta'^{18}O$ space, with relative humidity (RH) and turbulence parameter (n) as modelling parameters. Isotopic composition of marine moisture (δ_A) was assumed to be equal mean present-day values over North Atlantic at 30^{o}N [5]

II. Isotope and chemical evolution of recent infiltration water (technological water) introduced to the mine, which accquinted mineralization (dissolution of salts) and was undergoing evaporation, was modelled in the δ^2H-$\delta^{18}O$ and $\Delta^{17}O$-$\delta'^{18}O$ space, with relative humidity (RH) and turbulence parameter (n) as modelling parameters. Isotopic composition of atmospheric moisture (δ_A) as equilibrium vapour with shallow groundwater in the vicinity of the mine.



CONCLUSIONS

- **Multi-tracer approach adopted in studying the origin of mineral waters exploited in the Wysowa Spa revealed two separate mixing systems leading to the observed chemical and isotope composition of those waters. Three end-members are defined by: (i) highly mineralized diagenetic water of deep circulation, (ii) local infiltration water of pre-bomb (Holocene) age devoid of tritium, and (iii) recent infiltration water containing tritium.**
- **Negative $\Delta^{17}O$ value of the diagenetic end-member (ca. -15 per meg) may indicate evaporative marine environment in which clay minerals present in the Carpatian flysh were formed. Future, dedicated studies should clarify which process(es) leads to the observed $\Delta^{17}O$ signature of this water.**
- **Salt mines are vulnerable to water inflows from the surrounding geological formations. Stable isotope composition of brines constitute a powerful tool to trace the origin of water appearances in salt mines. Chemical composition of mine waters, although useful, cannot be used to distinguish between syngenetic (safe) and meteoric (potentially dangerous) water types occurring in such mines.**
- **Analyses of $\delta^{17}O$ and the secondary parameter $\Delta^{17}O$ provides additional constraints for the origin of water appearance in salt mines, delivering independent information about the origin and evaporation history of the analysed brine samples.**

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