

# Stable isotopes and hydrochemical data as a tool for identifying the origin of waters appearing in the Kłodawa Salt Mine (Poland)

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**Abstract:** Since 1975 about 185 isotopic analyses of water in a number of brine occurrences in the Kłodawa Salt Mine have been performed. Isotopic methods are shown to be a useful tool for identifying the origin of water. Four genetic groups are discussed: syngenetic brines, brines formed from infiltration water of warm pre-Quaternary climates, brines formed from water of Quaternary infiltration, and difficult to identify technologic and other waters.

## 1 INTRODUCTION

The Kłodawa Salt Mine is situated in central Poland, about 140 km west of Warsaw. It is located in the central part of a 60 km long salt structure piercing through the Mesozoic strata and forming a diapir 26 km long and 0.5-2 km wide. The clayey-gypsum cap up to 170 m thick covers the salt bed situated at the depth of 100-350 m, and is surrounded by the water-bearing Tertiary and Quaternary sediments. Below the Tertiary sediments, the diapir is surrounded by Mesozoic formations. Since the 1956 the salt has been exploited at four main levels (450, 525, 600 and 750 m) and several mid-levels, with the rate of  $6 \cdot 10^5$  tons/y. The total volume of excavations is about  $15 \times 10^6$  m<sup>3</sup> with typical dimensions of 120m×20m×20m. The total water inflow to the Kłodawa mine is about 18 l/h from the shafts and about 3 l/h from different water occurrences in mine workings. In 1995 almost 90 % of these occurrences appeared as a moist walls and drops of water, only 25 % occurrences are continuous, and six of them act as continuous inflows.

The isotopic composition of water occurrences in the Kłodawa mine has been monitored since 1975. Up to the end of 1999 about 185 samples were analysed for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in water in order to determine its origin. For most of the occurrences, the chemical analyses are also available. The isotope analyses were performed at the Faculty of Physics and Nuclear Techniques of the University of Mining and Metallurgy in Kraków, whereas chemical analyses by laboratory of the Kłodawa Salt Mine.

## 2 ANALYTICAL TECHNIQUES

Brine samples for oxygen isotope determination in water were prepared using standard procedure of equilibration with gaseous  $\text{CO}_2$  at controlled temperature of  $25.0 \pm 0.1$  °C. However, the duration of equilibration process was minimum 3 months. The  $\text{CO}_2$  was measured by mass spectrometer and the results obtained were corrected for major cation contents according to procedure described by Sofer and Gat (1975).

For analysis of deuterium content, brine samples were first distilled at temperature above 450 °C. Then water was reduced on metallic uranium at 650 °C, and the produced hydrogen was measured spectrometrically.

## 3 DISCUSSION

Results of stable isotope analyses are summarized in Figure 1. They can be divided into four main groups: syngenetic waters, palaeoinfiltration of warm climates, Quaternary infiltration, waters difficult to identify including technologic waters. For nearly all isotopically analysed waters, the chemical analyses were also available. In Figure 2a and 2b the equilibrium line and the results of chemical analyses are shown. It is evident that the sums of bivalent cations versus sums of monovalent cations are close to equilibrium line for almost all analysed brines over a wide range (Grabczak & Zuber, 1986).

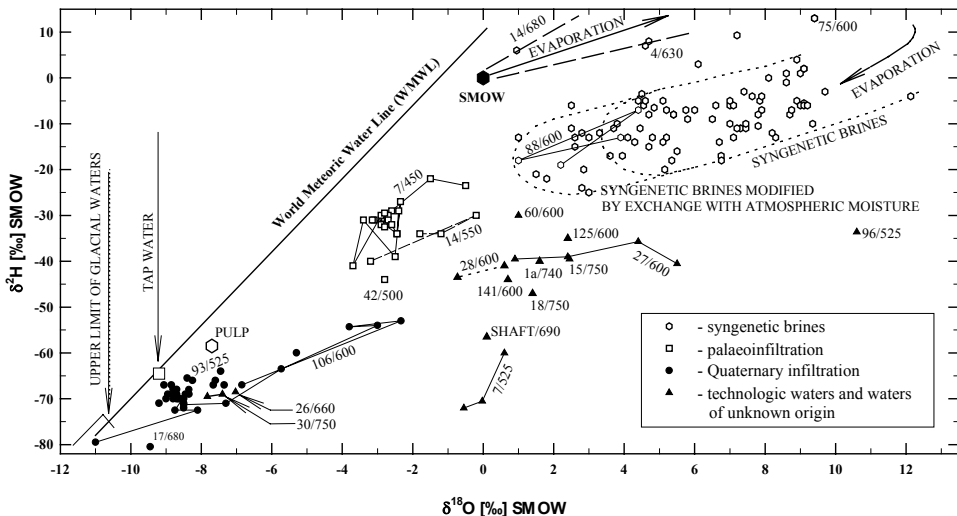


Figure 1 Isotopic composition of water inflows to the Kłodawa Salt Mine (most actual data). Notation A/B describes the order number of a given occurrence (A) and depth level of its appearance (B).

## **Syngenetic brines**

Only three occurrences (14/680, 4/630, 75/600, the first number indicating the

occurrence, and the second the depth level) can be classified as representing the

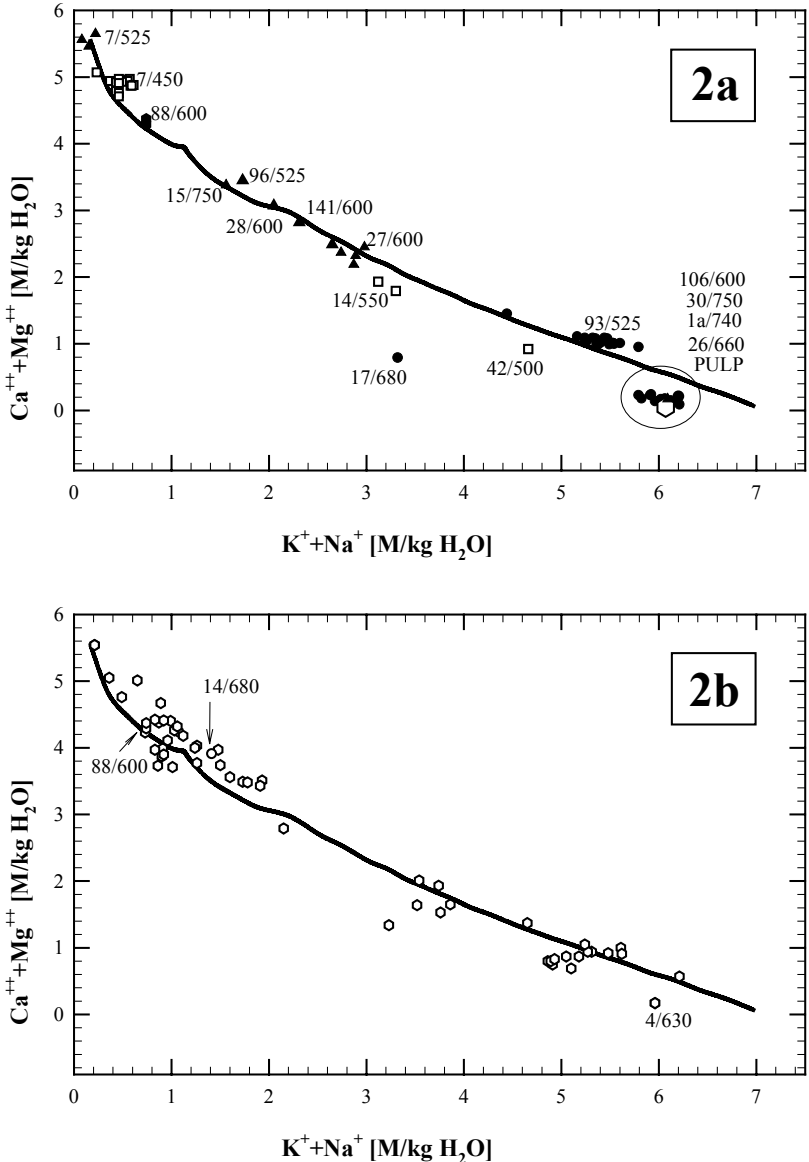


Figure 2 Sum of bivalent ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) versus monovalent ( $\text{K}^{+} + \text{Na}^{+}$ ) cations in brines *a*) brines containing water of pre-Quaternary and Quaternary infiltration as well as technologic water, *b*) syngenetic brines. Solid line represents proportion between sums of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  and  $\text{K}^{+} + \text{Na}^{+}$  concentrations at saturation for  $\text{NaCl} + \text{KCl} + \text{MgCl}_2 + \text{H}_2\text{O}$  in equilibrium with solid phase at  $25^{\circ}\text{C}$ .

early stage of ocean water evaporation. It is interesting that occurrences Nos. 14/680 and 4/630 have different proportions of bivalent and monovalent cations (Figure 2b).

Majority of analysed occurrences had isotopic composition corresponding to the end-stages of ocean water evaporation. Above 60 samples revealed isotopic composition covering the characteristic hook-shaped trajectory of evaporating ocean water. Some samples situated leftward the main hooked area represent syngenetic waters affected by isotope exchange with the mine atmospheric water vapour. The occurrence No. 88/600 is a typical representative of such process. Two points lie within the syngenetic waters area whereas two others are distinctly shifted to the left due to isotopic exchange with water vapour. That effect is especially strong when the flow rate is very low (long sampling time) and the collection of sample at the wall or roof is difficult to perform (e.g. brine drops and is collected below its appearance). The molecular and isotopic exchange with vapour was confirmed by tritium measurements in 1977. For instance, tritium was present in measurable amount in occurrences Nos. 66/525, 88/600, 75/600, 61/525, which represent syngenetic waters (Zuber et al., 1979). Chemical analyses shown in an approximate form indicate that some of the syngenetic brines have NaCl as a dominant component, which suggests no relation to the end stages of evaporation. However, the stable isotopes show unambiguously their syngenetic origin. Therefore, it may be concluded that their identification by chemical methods is not possible.

### **Brines of palaeoinfiltration (pre-Quaternary) origin**

The inflow 7/450 has existed since 1956. Its discharge decreased from 15 l/min at the beginning to 0.04 l/min in 1960. Its origin is supposed to be related to saline waters and brines of the Mesozoic formations around the salt diapir. These formations in central and northern Poland are known to contain mainly palaeoinfiltration waters of warm pre-Quaternary climates, lying slightly in right of the World Meteoric Water Line (Zuber & Grabczak, 1991). The isotopic composition of this water is additionally shifted to the right on the  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  diagram by isotopic exchange with water of crystallization in hydrated salt minerals during the migration in the diapir. The occurrence No. 14/550 which was active for three years had similar values of the isotopic composition.

### **Brines of Quaternary origin**

The inflow No. 93/525 appeared in 1985 in chamber 14. Its discharge has decreased from 30 l/h to about 10 ml/h at present. The initial isotopic composition of water was typical for Quaternary waters in central Poland in the  $\delta^2\text{H}$ - $\delta^{18}\text{O}$  diagram (Figure 1). However, the isotopic composition during the last 6 years has shown a shift characteristic for evaporated water reaching in 1999 the values of  $\delta^{18}\text{O} = -5.3 \text{ ‰}$  and  $\delta^2\text{H} = -60 \text{ ‰}$ , with a simultaneous decrease of monovalent cation content. That shift is related to a strong decrease of flow rate and possible evaporation both in the cavern, from which it flows, and on the chamber wall. Isotopic exchange with water of crystallization in hydrated salt minerals can also contribute to the shift observed.

The inflow No. 106/600 appeared in 1991 in central part of the mine, near a horizontal borehole which crossed the boundary of the diapir. The initial flow rate of 3 l/h dropped to the present, almost constant value of 2 ml/h. At the beginning the isotopic content was typical for glacial infiltration (strongly shifted to more negative values in comparison with tap water, Figure 1). With the decreasing flow rate the isotope composition was gradually changing to heavier values due to the effects described in the case of inflow No. 93/525. Waters at the end of the evaporation hook (Figure 1) are undoubtedly in isotopic equilibrium with hydrated salt minerals which precipitated from that water. It means that any water which exchanges isotopes with the water of crystallization in syngenetic minerals must have a tendency to be shifted in the direction of the end parts of the evaporation hook. Therefore both occurrences: No. 93/525 and 106/600 have a tendency to change their isotopic composition in that direction. Similar effects are observed for technologic water discussed further.

The inflow No. 17/680 was from a horizontal borehole, which crossed the boundary of the diapir. Fortunately, the borehole has been completely sealed.

### **Technologic waters**

The fourth group is represented by brines which are often difficult to identify. Technologic waters result as leaks from installations or as condensation water. They occur at the floor of mine workings. Due to their origin, the technologic waters may have isotopic composition close to waters of Quaternary origin (Nos. 26/660, 30/750, and pulp in Figure 1), or strongly shifted (Nos. 27/600, 28/600 and 125/600).

Some other occurrences, usually short-lasting, are especially very difficult to identify (e.g. Nos. 60/600, 125/600, 141/600, 1a/740, 15/750, shaft/690, 7/525, and 96/525). Their origin remains unclear, however, as they occur less frequently than all the other brines, that limitation of the isotope method is not very significant.

In Figure 2 the contents of the main cations in investigated brines are shown. Within the accuracy of determinations all the results are close to the saturation line, except of No. 17/680 which, as mentioned, was from the horizontal borehole which crossed the boundary of the diapir. Surprisingly, a number of syngenetic brines with the isotopic composition corresponding to the end stages of the ocean evaporating water, have the dominant content of the monovalent cations. Therefore, chemical composition cannot serve for the identification of the origin of water, though sometimes is helpful in combination with isotope analyses (Grabczak & Zuber, 1986).

## **4 CONCLUSIONS**

The isotope method has appeared to be very useful in identification of the origin of mine brines in spite of some limitations resulting from: a) effects occurring

prior to sampling, b) the presence of technologic waters, and c) the presence of some occurrences difficult to identify.

## REFERENCES

- Grabczak J. & Zuber A., 1986. A combined isotope and chemical approach to determining the origin of brines in salt mines. *Freiberg. Forschungsh.*, C417, 105-115.
- Sofer Z. & Gat J.R., 1975. The isotope composition of evaporating brines: effect of the isotopic activity ratio in saline waters. *Earth Planet. Sci. Lett.*, 26, 179-186.
- Zuber A., Grabczak J. & Kolonko M., 1979. Environmental and artificial tracers for investigating leakages into salt mines. In: *Isotope Hydrology 1978*, vol. I, IAEA, Vienna, 45-63. Zuber A. & Grabczak J., 1991. On the origin of Mesozoic brines in central and northern Poland (in Polish). In: *Współczesne Problemy Hydrogeologii*. Wyd. SGGW-AR, Warszawa, 202-207.

Izotopy trwałe i dane hydrochemiczne jako narzędzie identyfikacji źródła wody pojawiającej się w kopalni soli w Kłodawie (Polska)

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**Streszczenie:** Od 1975 roku do chwili obecnej wykonano około 185 analiz izotopowych wody w kilku obszarach wypływu solanki w kopalni soli w Kłodawie. Metody izotopowe okazały się przydatne dla określenia pochodzenia wód kopalnianych. Przedstawiono cztery grupy genetyczne: solanki syngenetyczne, solanki powstałe z infiltracji wody w ciepłych klimatach przedczwartorzędowych, solanki pochodzące z infiltracji wód czwartorzędowych, oraz trudne do zidentyfikowania wody technologiczne