APPLICATION OF STABLE ISOTOPES ($^{18}$O, D) TO STUDY THE PROVENIENCE OF MINERAL WATERS FROM SOME LOCATIONS OF ROMANIA*

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The isotopic study ($^{18}$O, D) of mineral waters from some locations (Bucovina, Covasna, Tusnad and Someseni) of Romania was realised in tentative to identify its origin. The investigations of waters from Bucovina, Covasna and Someseni (Springs No. 1, 2, and 15) confirms the meteoric provenience, having the deuterium content of meteoric water, but shifted to higher $^{18}$O content. This $^{18}$O shift is the result of isotopic exchange of the water oxygen with the rocks oxygen in its trajectory to the discharge.

The Spring No. 8 waters from Someseni Spa and Tusnad waters present the water isotopic content of mixed deep water with shallower meteoric water having higher isotopic (D, $^{18}$O) content. The Spring No. 3 waters from Someseni Spa present the springtime isotopic pulse, like a Becas brook, with water depletion in D and $^{18}$O isotopes proving pollution with surrounding snow water.

Key words: isotopic study ($^{18}$O, D), Romanian waters, deuterium, oxygen-18.

1. INTRODUCTION

The provenience study of mineral waters from some locations of Romania (Bucovina, Covasna, Tusnad and Someseni) was realised with water stable isotopes $^{18}$O and D.

The meteoric origin of the waters in the isotopic studies is proved by isotopic values of: General Meteoric Water Line (GMWL), Local Meteoric Water Line (LMWL), and Geothermal Water Line [1]. The diagram (dD, d$^{18}$O) represents a Craig line with slope $s = 8$, and an intercept $d = 10$ (deuterium excess).

Local precipitation (LMWL) lies on straight line with slope close to 8, as a parallel of GMWL.

The Geothermal Waters Line shows deviation in $^{18}$O whereas the D content remains unchanged.

Evaporating bodies of water lie also on straight line, with variable slopes (2–5), and variable intercept with meteoric water line. This intercept is the isotopic content of the water before evaporation started.

The isotopic study ($^{18}$O, D) of mineral waters from some locations of Romania (Bucovina, Covasna, Tusnad and Someseni) was realised in tentative to identify his origin.

2. RESEARCH METHODS

The $^{18}$O contents of water was measured by CO$_2$ equilibration method with ATLAS 86 mass spectrometer equipped with double collection and double introduction line.

The deuterium analyses of water were carried out with the home-made mass spectrometer SMAD-1, on the hydrogen gas obtained by in line quantitative reduction of water sample (about 1 $\mu$l).

The isotopic contents were expressed as $\delta I$ value, in “part per thousand”,

$$\delta I = (R/R_S - 1)1000,$$

where: $I$ represents D, or $^{18}$O isotopes; $R$ – the isotopic ratio of sample; $R_S$ – the ratio of international V-SMOW standard (Vienna Standard Mean Ocean Water). The precision in $\delta^{18}$O measurements was $\pm 0.3 \permil$. The precision of $\delta D$ values was $\pm 2 \permil$.

3. RESULTS AND DISCUSSIONS

The $\delta D$-$\delta^{18}$O diagrams for Bucovina waters are presented in Fig. 1. This diagram shows the meteoric origin of mineral waters DOMAROM, and Lebes Spring having the average deuterium content of local meteoric water. The deeper circulation of these waters was proved by O-18 shift to higher values, the line Deep Water Isotopic Shift on the Fig. 1. The isotopic content of mineral waters was higher as compared with the isotopic content of the local meteoric water, as Moldova River Water (The Horizontal Line of Springtime Isotopic Shift in Fig. 1).

The diagram in Fig. 2 shows the isotopic complex picture of waters from Covina County. The waters S1 VITAROM, S2 VITAROM, S3 VITAROM, FIV RMIN, and FI IAFA presents his origin in meteoric water having average deuterium content of local meteoric water, Fig. 2. The O-18 contents (Deep Water O-18 Shift line, Fig. 2) were different, from deep meteoric (S1 VITAROM, and FI IAFA) to Geothermal Water Like (S2 VITAROM, S3 VITAROM, and FIV RMIN). The isotopic contents of waters FII IAFAA, and
Fig. 1. – δD vs. δ18O waters diagram of Bucovina County.

Fig. 2. – δD vs. δ18O for waters from Covasna County.

FVII HOTEL DACIA are higher as compared with Deep O-18 Shift, Fig. 2. He positions on (δ18O, δD) diagram shows the origin in a mixing process of deep
water with shallower water (having higher isotopic contents). The Springtime Isotopic Shift is also observed in Fig. 2 similar to Fig. 1.

The isotopic investigation of mineral waters from Someseni Spa by deuterium analyses have presumed that these waters are related to a unique aquifer, and the differences in the physical and chemical properties of the sources are related to the different ways in which these waters are followed in the vicinity of the salt body [2]. These waters also were investigated by O-18 and deuterium for a short time period, January, and February 2001[3] characterized by insignificant precipitation. Present study (October 2003 – March 2004) of Someseni Spa waters shows the complex isotopic picture of these waters resulting in different ways of mixing the deep waters of meteoric origin with surrounding, shallower waters.

The δD vs. δ18O in waters investigations of 1, 2, 8, and 15 springs from Someseni Spa area confirms the meteoric provenience. His deuterium content is the mean deuterium content of local meteoric water (Somes River water), but shifted to higher 18O content, Fig. 3. This 18O shift is the result of isotopic ex-

![Fig. 3. – δD vs. δ18O in waters from Someseni Spa area.](image-url)
change of the water oxygen with salted layers oxygen in its trajectory to the discharge. The linear regression study of $\delta D - \delta^{18}O$ lines from springs No. 1, No. 2, and No. 15 with similar slopes ($s_1 = 1.14$, $s_2 = 1.25$, and $s_{15} = 0$) and deuterium excesses ($d_1 = -62$, $d_2 = -62.2$, and $d_{15} = -70.31$) confirms the meteoric origin with small mixing with shallower meteoric water.

The water of Spring 8 presents a small mixing of deep water with shallower water. The water line from Spring No. 3 presents a slope typically for local evaporation water line. The springtime isotopic pulse of Spring No. 3, as in Becas Brook waters, with water depletion in D and $^{18}O$ isotope, proving provenience in surrounding snow waters, is also present in Fig. 4.

Fig. 4 shows the meteoric origin of mineral waters from “Tusnad Nou” spring, having the deuterium content of average meteoric water (Deep Water O-18 Shift line level in the Fig. 4), shifted to higher $^{18}O$ content similar with geothermal waters. The isotopic content of local meteoric water (represented by isotopic content of Olt River water) is higher as compared with this value from mineral water. The higher values of isotopic contents in water from Olt river come from summer precipitation.

Fig. 4. – The proved meteoric origin of Tusnad waters by O-18, and D isotopes.

4. CONCLUSIONS

The waters investigated proved a meteoric origin, including whole spectrum of variation. The typical of meteoric origin are the waters from: Moldova River, Covasna County drinking water, Covasna River, Olt River, and Somesul Mic
River. The Geothermal Water Like waters come from: Bucovina (Domarom, and Lebes); Covasna (S1 VITAROM, S2 VITAROM, S3 VITAROM, FIV RAMIN, and FI IAFA), and Someseni (Spring No. 15). The isotopic contents of waters from: Covasna (FII IAFA, and FVII HOTEL DACIA), Someseni (No. 1, 2, 3 and 8 springs) were the result of mixing process of deep waters with shallower waters.

REFERENCES