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Origin of mineral waters from Someseni, Transylvanian Basin, Romania

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Analysis of the stable isotope composition of the mineral waters from Someseni, Transylvanian Basin, Romania has been made to constrain their origin. The mineral-rich aquifer is located on the western border of the Neogene Transylvanian Basin. The isotopic study (^{18}O, D) of mineral waters from Someseni Spa was carried in order to rehabilitate them as natural curative waters. Water samples from five springs (1, 2, 3, 8 and 15), from Becas Brook and from River Somes were collected monthly from October 2003 to March 2004. The quantity of precipitation and the mean temperature in the area were monthly recorded. The deuterium *vs.* ^{18}O investigations of the springs indicate a meteoric provenance with deep circulation, having the deuterium content of meteoric water, but shifted to a higher ^{18}O content as result of isotopic exchange with country rock. The D and ^{18}O values for springs 3 and 8 in February 2004 and March 2004 respectively, suggest some influence of surface waters derived from melting of the snow cover.

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INTRODUCTION

The study of the characteristics and origin of groundwaters has been among the most successful areas for the application of natural stable isotope abundance variations. This is largely due to the conservative nature of the stable isotope composition of water in an aquifer, as a result of which it is possible to characterize the origin of waters unambiguously: groundwaters "remember" the isotopic composition of their origin over long periods, of the order of ten thousand years, provided they are not exposed to temperatures above 60–800°C. Meteoric waters are derived directly from precipitation or from fresh surface waters, usually by recharge through an unsaturated soil zone. The isotopic composition of the meteoric groundwaters generally matches that of local precipitation, at least in the humid climate zone. When aquifer temperatures reach values of 800°C or more, a rapid change of stable isotope composition of the waters occurs so that this composition no longer corresponds to their original one. This process is characteristic of geothermal settings (Gat and Gonfiantini, 1981).

The match between the isotopic composition of precipitation and that of the groundwater derived from it is, however, by no means perfect. Changes in isotopic composition occur, mainly due to the recharge process. To a lesser extent, they come about as a result of non-conservative behaviour of water in the aquifers, through interaction with rock components or mixing with groundwaters from different sources.

Here, we study the stable isotope composition of groundwaters to determine the origin of mineral waters from Someseni in the Transylvanian Basin, Romania.

The therapeutical qualities of mineral waters from Someseni have been known since the early 1920's. The spa was established in 1927 when exploration drilling began. On a surface of less than 1 ha, there were established more than 35 mineral water sources with different yields and concentrations, of considerable curative potential. The spa began its slow decay in the mid 1970's, so that by the late 1980's it was practically derelict other than its medical components. Only five of the springs can be sampled currently. This isotopic investigation of mineral waters from Someseni Spa is an essential part of an effort to rehabilitate them as natural curative waters.

The first scientific study of the mineral waters from Someseni was completed in the early 1920's, focussing on their chemical composition and medical properties. A subsequent study concerned their radioactivity (Szabo, 1954). Studies of the Someseni mineral water dynamics followed (Pricajan, 1972; Baciu *et al*., 2001). The isotopic investigation of these waters began in 2000, and initial analyses of their deuterium content has been reported (Cuna *et al*., 2001).

MATERIALS AND METHODS

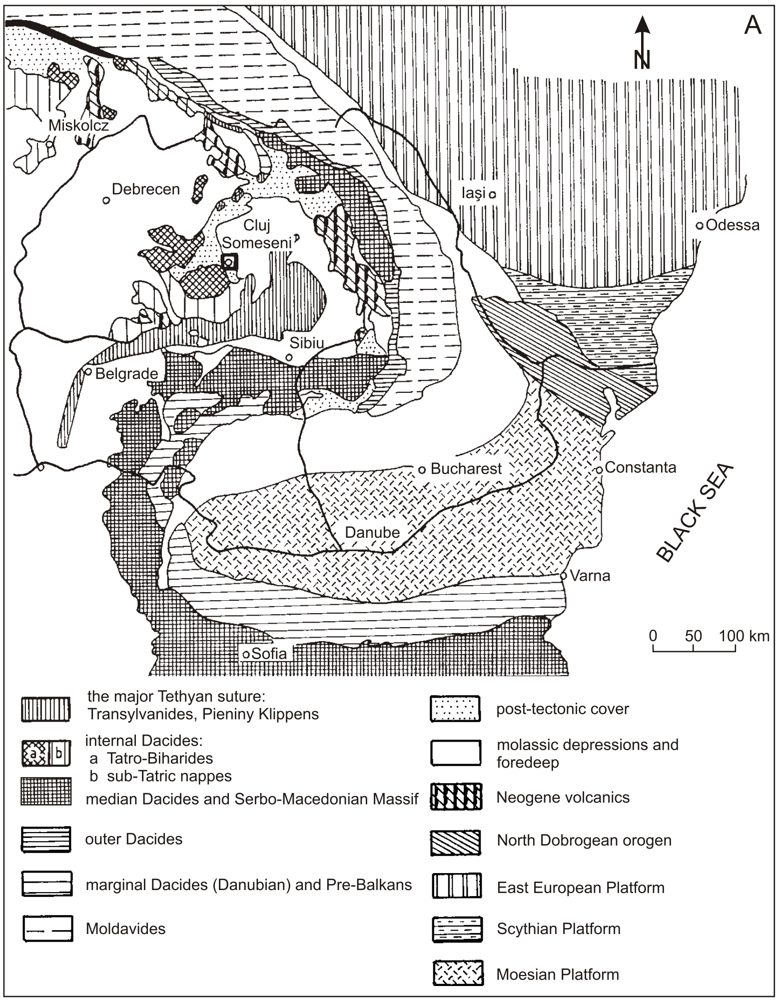
STUDY AREA

The area studied, Someseni Spa, is located in the eastern part of Cluj-Napoca city (Romania), at the contact between the alluvial plain and the first terrace of the River Somesul Mic. Geologically, the aquifer is located on the western border of the Neogene Transylvanian Basin (Fig. 1). In this area, the Neogene deposits gently dip to the east and are affected by a number of folds related to mid-Badenian salt tectonics.

The Transylvanian Basin (TB) contains molasse sediments of Neogene age, reaching a thickness of 4000 m in the centre of the Transylvanian Depression (TD). The term Transylvanian Depression refers to the Neogene sedimentary basin while the term Transylvanian Basin includes deposits back to the Mid-Cretaceous. The TB is superimposed on two older tectonic units, namely a folded basement and its post-tectonic cover. The location of the TB in the Carpathian-Panonian system is shown on Figure 1. The basement is a segment of the main Thetyan suture and consists of metamorphic nappes of the internal and median Dacides, overridden in the west-central area by the ophiolitic suite which marks the suture (Sandulescu, 1988). The post-tectonic cover consists of 4000 m thick Late Cretaceous, Paleogene and Eo-Miocene deposits. The Someseni spring area is situated in the axial zone of an anticline with a salt core. Marls with frequent sandstone and volcanic tuff intercalations dominate the local lithology of these deposits. The alluvial deposits of the river generally cover the Neogene strata (Baciu *et al*., 2001).

SAMPLES

Water samples from five springs (1, 2, 3, 8 and 15), from Becas Brook as well as from the River Somes, were collected monthly in sealed glass bottles between October 2003 and March 2004. The quantity of precipitation and the mean temperature in the area were recorded every month (Table 1). The mean annual temperature of the springs at surface is 16°C. Al-



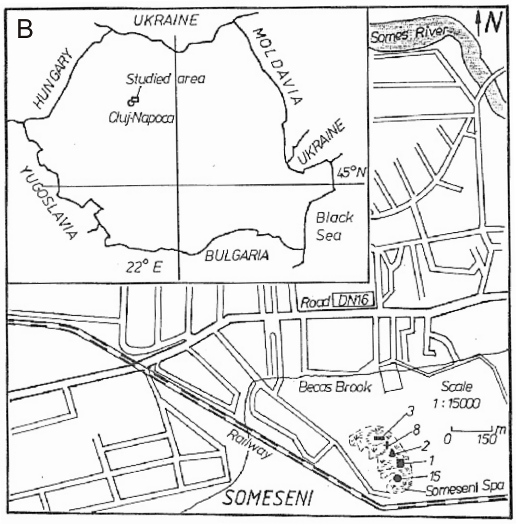


Fig. 1A — the general tectonic framework of the Transylvanian Basin (tectonics after Sandulescu, 1984), rectangle denotes the study area; B — location sketch of the springs (1, 2, 3, 8 and 15) in the Someseni Spa

Table 1

The quantity of precipitation and the mean temperature

Month/year	Precipitation [mm/month]	Mean temperature [°C]
October/2003	58	7.1
November/2003	38.5	4.6
December/2003	12.7	–2.4
January/2004	41.8	–4.4
February/2004	35.8	–1.1
March/2004	27.7	4.4

though these waters are not geothermal, we presume that aquifer temperatures reach values of 80°C or more at depth.

The waters from these springs are of different chemical compositions as well as possessing different therapeutic effects. The total dissolved solids (TDS) contents of the five springs are in the range of 2.5 to 20 g/l. The chemical composition belongs to the sodium-chloride type. The dominance of Na^+ and Cl^- ions is stronger as the concentration increases (Table 2). The chlorinated, carbonated, sodium, calcium and lithium-laden water may be used for drinking with digestive-diuretic effects. Another characteristic of these waters is the radon content of about 35 Bq/l (Baciu *et al*., 2001).

METHODS

The ^{18}O contents were measured by equilibration of 3 ml water with CO_2 and measurement of the isotopic ratio of CO_2 using an *ATLAS 86* mass spectrometer equipped with a double collector and double inlet system (Epstein and Mayeda, 1953; Cuna and Marca, 1996). The deuterium analyses of water were carried out with a home-made mass spectrometer *SMAD-1* on the hydrogen gas obtained by on-line quantitative reduction of about 1 ml water sample (Berdea *et al*., 1992).

The isotopic contents were expressed as δI value in "parts per thousand":

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

where: I — D or ^{18}O isotopes, R — the isotopic ratio of sample, R_S — the ratio of international V-SMOW (Vienna Standard Mean Ocean Water) standard (Craig, 1961; Gat and Gonfiantini, 1981*a*); the precision of $\delta^{18}O$ measurements is ±0.2‰; the precision of δD values is ±2‰.

RESULTS AND DISCUSSIONS

The results of the deuterium and oxygen-18 measurements of waters from five springs (1, 2, 3, 8 and 15), Becas Brook and River Somesul Mic are given on Figure 2. The average content of local precipitation for deuterium and for oxygen between October 2003 and March 2004 was –73‰ and –10.3‰ respectively. The δD in water of springs 1, 2, 3, 8 and 15 support a meteoric provenance, having a deuterium content similar to that of the local meteoric water (Fig. 3), but shifted to higher ^{18}O contents (Fig. 4). From the deuterium analyses we presumed that these waters are related to a unique aquifer. The observed differences of the physical and chemical properties (Table 2) are interpreted as due to different pathways taken by the waters to the surface.

The water samples from the River Somesul Mic fall on, or close to, the MWL (Meteoric Water Line) indicating that these waters are of meteoric origin and are not affected by secondary isotopic effects such as evaporation (Fontes, 1980; Gat and Gonfiantini, 1981*b*; Hoefs, 1987). The water samples from

Table 2

The chemical composition of the water samples

Chemical composition [mg/l]	Spring 1	Spring 2	Spring 3	Spring 8	Spring 15
Cl^-	1039.1	1875.3	11182.5	2397.6	1044
Br^-	0.4	0.05	–	–	–
NO_3^-	8.4	8.3	–	1.8	0.7
SO_4^{2-}	165.4	246	547.3	300.2	96.7
HCO_3^-	484.9	536.8	610	506.3	488.2
Na^+	653.9	1309.2	7431	1718.4	650.1
K^+	24.3	14	$(Na^+ + K^+)$	12.1	43.6
Li^+	0.4	0.4	–	0.2	2.2
Ca^{2+}	172.4	161.9	246.1	120.4	158.2
Mg^{2+}	37.9	18	16.6	12.8	21
Fe^{2+}	0.1	1.2	–	1.6	5
TDS	2640	4217.25	20051.9	5109.4	2556.2

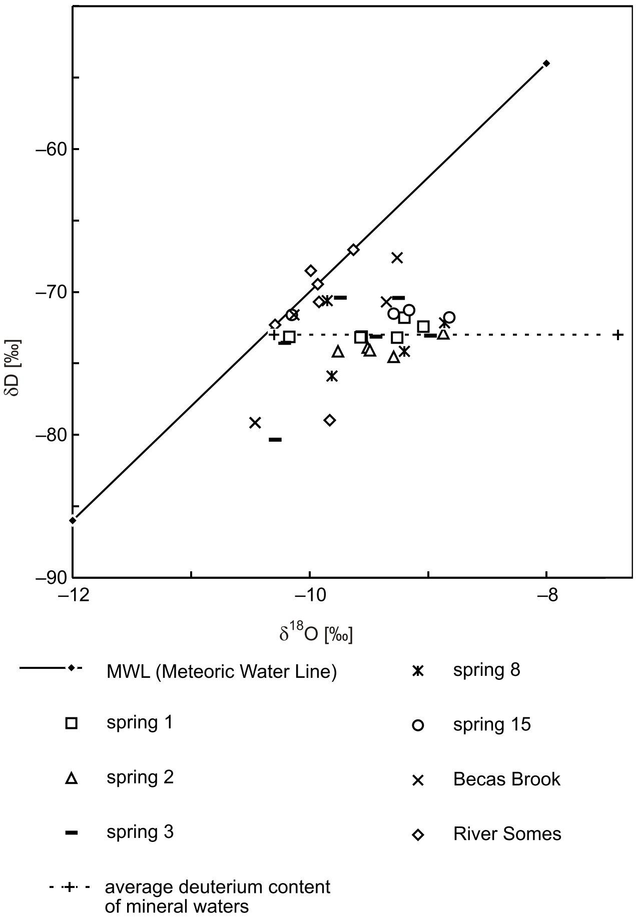


Fig. 2. δD *vs.* δ^{18}O in waters from Someseni Spa area

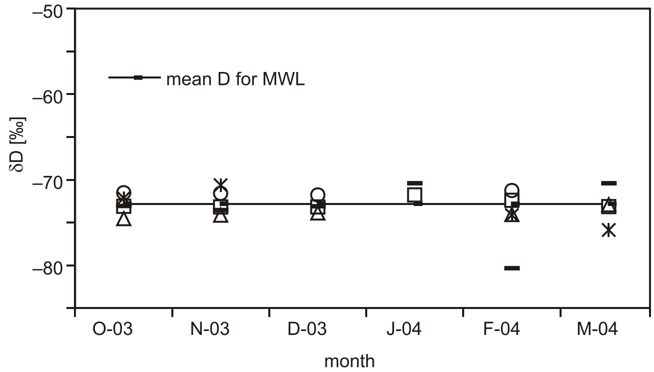


Fig. 3. The seasonal variations of δD

O-03 — October 2003, N-03 — November 2003, D-03 — December 2003, J-04 — January 2004, F-04 — February 2004, M-04 — March 2004; other explanations as on Figure 2

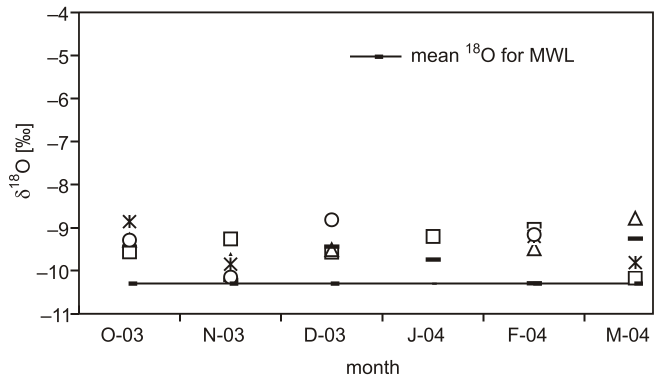


Fig. 4. The seasonal variations of δ^{18}O

Other explanations as on Figures 2 and 3

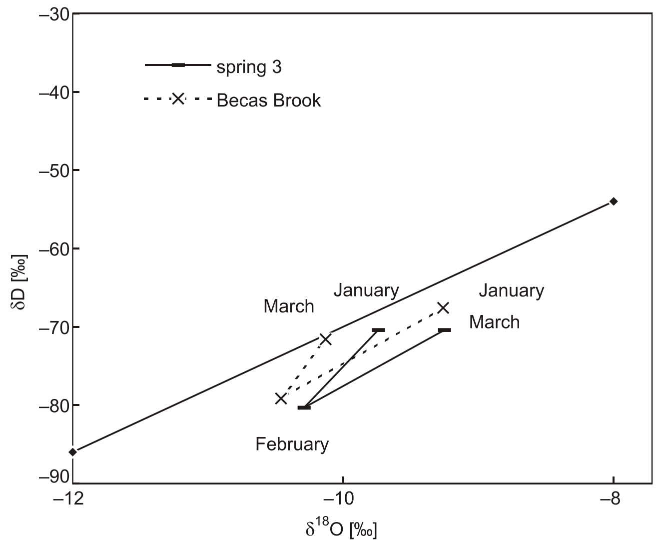


Fig. 5. The winter isotopic pulse of spring 3 and Becas Brook waters

Other explanations as on Figure 2

Becas Brook fall close to the MWL, but there is some scattering of δ^{18}O for these water samples. Over the period of sampling, the Becas Brook waters appeared to have been polluted with organic compounds and waste. We have correlated this scattering with organic pollution of these waste waters.

Generally, the more depleted values of δD and δ^{18}O are due to the contribution of snow melt, as elsewhere (Ahmad *et al.*, 2003). The waters from the River Somesul Mic show a winter isotopic pulse in March and the waters from Becas Brook show such depleted values in February. The mean temperature in February and March is consistent with melting snow (Table 1) and explain this isotopic pulse.

There is an unexpected depleted δD value for spring 3. This value was observed in February when Becas Brook waters showed an isotopic pulse due to the contribution of meltwater from snow. It seems that the water from spring 3 was admixed with water originated from melting of snow cover. In Figure 5 are shown the winter isotopic pulse of the Becas Brook waters, and the similar isotopic pulse of water from spring 3. These data indicate that some infiltration occurs, and that we have to study better this area in the future. For example, we could correlate the isotopic composition of these waters with their chloride content. Chloride, as a conservative constituent in groundwater, should reflect mixing processes between shallow infiltration water and deep circulating water (Payne *et al.*, 1979).

The monthly variations of $\delta^{18}O$ for the five springs are shown in Figure 4. As we suggested for δD, there is an isotopic pulse $\delta^{18}O$ for the spring 3 indicating the influence of water originated from melting of snow cover. The δD and $\delta^{18}O$ values for spring 8 in March 2004 also suggest some influence of surface waters. The springs 3 and 8 both have a small flow at discharge and their surroundings were saturated with surface waters. These springs, especially spring 3, are partly blocked, and they have to be drained and the surroundings kept clean and dry. In this way is quite possible to diminish the surface-water infiltration and to eliminate surface-water/groundwater influences.

Such a small influence becomes visible for springs 3, 8 and 15 in November 2003 when the isotopic composition of water was depleted in ^{18}O. It could be the effect of the higher quantity of precipitation in October 2003 (Table 1), followed by some infiltration to the damaged areas around the springs.

For the five springs there is an evident shift in ^{18}O to higher values that could be explained either by isotopic exchange at high temperatures occurring within the bedrock (Clayton and Steiner, 1975) or at normal temperatures by chemical or mineralogical reactions involving the water and the rock (Samuel, 1980). We presume that the ^{18}O shifts toward heavier values are the result of the non-conservative behaviour of the water in the aquifer through interaction with rock components which contain oxygen. Water and rocks are generally in isotopic disequilibrium and therefore tend to exchange their isotopes in order to approach equilibrium. The extent of exchange depends on the initial ^{18}O content, on the specific water-mineral fractionation factors which are temperature-dependent, and on time and the extent of surface contact. This process is effective only for oxygen, the hydrogen content of rocks generally being too low to significantly affect the isotopic composition of the groundwaters (Sheppard, 1986).

CONCLUSIONS

The isotopic investigations of five springs from Someseni Spa confirm a meteoric provenance, having the deuterium content of local meteoric water and shifted to higher ^{18}O contents.

The measurements confirm the previous studies showing that all the springs are related to a unique aquifer. The observed differences of the physical and chemical properties are interpreted as due to different pathways the waters have followed to the surface.

The water samples from Becas Brook fall close to the MWL, but there is some scattering of $\delta^{18}O$ for these water samples. We have correlated this scattering with organic pollution of these waste waters.

The highly depleted values of δD and $\delta^{18}O$ for the River Somesul Mic and Becas Brook are due to the contribution of snow melt (winter isotopic pulse). We explain the depleted δD value for spring 3 in February 2004 by admixing with water originated from melting of snow cover. These data indicate that some infiltration occurs, and that we have to study better this area in the future. The δD and $\delta^{18}O$ values for spring 8 in March 2004 also suggest some influence of surface waters. Springs 3 and 8 both have a small flow at their discharge and their surroundings were saturated with surface waters. These springs have to be drained and the surroundings kept clean and dry to be suitable for medical use.

The $\delta^{18}O$ shift toward higher values for the five springs is the result of interactions and isotopic exchange of oxygen from water with rock matrix which contains oxygen.

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