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Radiocarbon Ages of Mineral and Thermal Waters of Slovakia

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Abstract: The sources of mineral and thermal waters (MTW) are on the territory of central Slovakia mainly in the Inner Carpathians depressions and/or at margins of lowlands. The springs are always bound to crossing of longitudinal (older) and transversal (younger) faults. The aquifers of MTW are formed by Triassic limestones and dolomites, which are found in the mountains as well as in the pre-Tertiary substratum of depressions and lowlands. MTW occur in Triassic carbonates of envelope and nappe units, and they are of artesian and/or open structures. Travertines have been deposited from many MTW springs. Therefore the ages of travertines indicate the periods when these waters were formed. The ages of travertines from 24 localities with 61 deposits were estimated by paleontological finds and by radiocarbon dating. The radiocarbon ages plus ^{18}O and ^{13}C of MTW were determined in samples from 43 localities with 61 sources. At present, there are only boreholes available, as natural outflows have already been caught by them. A comparison of all the available data, also regarding the snow line changes during the last 35 000 y, was carried out with the aim to draw conclusions on MTW flow development during the Quaternary period. The time interval of MTW flows from their recharge to discharge areas was evaluated by means of radiocarbon dating as well. The analysis of all the available data resulted in the conclusion that MTW in Slovakia began to issue 2 million years ago at the end of the Late Pliocene, and they were increasingly flowing mainly during interglacial periods. The radiocarbon ages of MTW vary within the interval of 32 000 and 9 000 y. Consequently, the present-day waters might be recharged during the Würm 2 3 and Würm 3 Interstadials and the Holocene period.

1. Introduction

Radiocarbon dating of groundwater, mineral and thermal waters has been a widely used method applied in hydrogeological studies (e.g. Vogel and Enhalt, 1963; Geyh and Wendt, 1965; Vogel, 1970; Geyh, 1991; Geyh, 2004). However, there has been an absence of such investigations in the Inner Carpathian region. The sources of mineral and thermal waters (MTW) are mainly on the territory of Central Slovakia. The majority of springs outflow in the Inner Carpathian depressions and/or at margins of lowlands. The issues of waters are bound to marginal faults between the mountains and depressions and/or lowlands. A less amount of issues is bound to horsts (elevations) of the pre-Tertiary substratum inside depressions and lowlands. The springs are always bound to crossing of longitudinal (marginal, i.e. older) and transversal (younger) faults. The aquifers of MTW are formed by Triassic limestones and dolomites, which are found in the mountains as well as in the pre-Tertiary substratum of depressions and lowlands.

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The Western Carpathians are part of the Alpine – Himalayan folded mountain system. The core crystalline rocks units are overlaid by sediments of envelope units that are covered by 2 to 3 nappes (lower, middle and upper). MTW occur in Triassic carbonates of envelope and nappe units (Franko and Melioris 1999). There are artesian and/or open structures of MTW.

The present-day relief of the territory (mountains – depressions) started to develop during the Neogene (in the Badenian) mainly, however, in the Pliocene, and this neotectonic stage has been lasting till now (Lukniš and Plesník 1961). In this stage the system of intramontane depressions (basins, lowlands) has been formed, which continued in development in the Pliocene and Quaternary. The depressions are connected with movements at marginal faults, along which the mountain ranges have arisen. With more intense movements in the Pliocene also the first outflows of MTW to the end of the Late Pliocene are connected, from which travertines deposited. At present, there are practically only boreholes as natural outflows are already caught by them. Only 17 boreholes from 44 catch MTW at places where they have never outflowed.

Changes in climatic conditions took place and cold (glacial) and warm (interglacial) periods alternated at the beginning of the Quaternary. In cold periods terraces and loesses formed and mineral waters issued and travertines deposited from them (Ložek 1973) in warm periods. In the glacials the territory of Slovakia was covered by tundra vegetation. In the interglacials the tundra retreated to the north and the territory under study was covered by forests (Lukniš and Plesnik 1961). The geological age of travertines is summarised in a most complex way in the monographic works by Ivan (1943), Kovanda (1971) and Vaškovský (1977). As travertines have been deposited from many springs of MTW, their age indicates the periods when these waters have issued.

The aim of the present study was to investigate distribution and ages of MTW observed in the Central Slovakia. Therefore, relative and geologic ages of travertines were estimated, and MTW were analysed for ^{14}C and stable isotopes (^{18}O and ^{13}C). A comparison of the available data, also regarding the snow line changes during the last 35 ky, was carried out with the aim to draw conclusions on mineral and thermal water flow development during the Quaternary period.

2. Sites and methods

The map with sampling sites of MTW and deposits of travertines in Slovakia is shown in Fig. 1. The issues of waters are bound to marginal faults between the mountains and depressions and/or lowlands (Fig. 2). Relative and geologic ages of travertines were estimated at 24 sites with 61deposits. MTW were sampled at 43 localities with 61 wells. Description of the wells is presented in Table 1.

Water samples for radiocarbon analysis of 100 L volume were collected directly from the source. Bicarbonates were extracted as soon as possible by coagulation with barium chloride. In the laboratory, carbon dioxide was released then from barium carbonate by addition of H_3PO_4. Methane synthesised from carbon dioxide was used as a filling gas of the low-level proportional counter. Measuring time of samples was from forty to sixty hours. In addition to each water sample also samples of background and of radiocarbon standard (NIST Oxalic Acid) were measured. A few mL of carbon dioxide liberated from the $BaCO_3$ sample were analysed using a mass spectrometer for the determination of the isotopic ratio of $^{13}C/^{12}C$ and $^{18}O/^{16}O$, which are expressed as ^{13}C values relative to the PDB standard, and ^{18}O data are reported against the VSMOW standard. The procedures used have already been published (Povinec, 1972; Povinec, 1980; Michalko, 1999) therefore they will not be described here.

Radiocarbon apparent age of water was calculated according to the relation:

$$t \quad \frac{T_{1/2}}{\ln 2} \ln \frac{A_0}{A_t},$$

where $T_{1/2}$ is the half-life of the radiocarbon decay, A_t is the activity of the sample at the time of sampling, and A_0 is the activity of the standard sample adjusted for the time equal to zero. In the calculation of the radiocarbon apparent age of groundwater samples we came out from the empirically confirmed assumption that the initiative radiocarbon activity of bicarbonates in the investigated water during the period of its infiltration was 85 percent of modern carbon (85 pmc) (e.g. Vogel, 1970). Groundwater samples with radiocarbon activity higher than 85 pmc could be then considered as contemporary.

3. Results

Relative ages of travertines

The relative ages of travertines (e.g. oldest, older, old, young, younger, youngest) were considered according to their disintegration. The examples of such evaluations are presented in Fig. 3. Disintegration arises by frost, pressure of glaciers, karstification and slope movements. It is visible from Fig. 3 that the greatest disintegration is observed in the travertines of Dreveník from Spišské Podhradie, which are broken up into individual blocks. To less extent the travertines of Pažica, also from Spišské Podhradie, are disintegrated. Less disintegrated are travertines of Horbek in Vyšné Ružbachy and least those of Hrádok in Gánovce. According to the relative ages of travertines, we may then also evaluate the relative ages of MTW, as travertines deposited from them.

Geological ages of travertines

The geological ages of travertines are summarised in Fig. 4. We may state that MTW started to issue earliest at 6 deposits of travertines in the Late Pliocene dated back 2 My. Further outflows of waters are concentrated to the Günz-Mindel (4 deposits), Mindel-Riss (7 deposits) and Riss-Würm (10 deposits) Interglacials. One deposit of travertines is bound to the Günz 1 2 Interstadial and 3 deposits to the Würm 1 2.

The outflows of MTW continued in the Holocene at all the localities or in their surroundings. It is to be seen from Fig. 4 that with later and later interstadials and interglacials the number of water outflows was generally higher and higher. As travertines have been deposited from many springs of mineral and thermal waters, their age indicates the periods when these waters have issued.

Radiocarbon apparent ages of MTW

The results of the isotope analyses of the water samples are presented in Table 2. The radiocarbon apparent age and also the radiocarbon activity of the samples are presented with the standard deviation of 1 . Concentrations of carbon ^{13}C show that in most cases carbon in bicarbonates in the investigated waters is isotopic heavier than it is usual in plain ground waters. ^{13}C values in groundwater are usually from 10 to 18 ‰ (Vogel and Ehhalt, 1963). In the investigated waters ^{13}C values are higher. Such ^{13}C values suggest that besides CO_2 of atmospheric origin also CO_2 of mantle (juvenile s. l.) origin take part in production of bicarbonates in the investigated waters. Mantle origin of free CO_2 is also confirmed by ^{13}C values if they are higher than –7 ‰ (Cornides and Kecskes 1982). These ^{13}C values indicate that the resultant radiocarbon age of the analysed waters can be biased in such a way that it is higher than the real time of retardation of the groundwater. Contamination by the inactive carbon (CO_2 of mantle origin) causes smaller standard deviations than contamination by contemporary CO_2 of atmospheric origin. The contamination by 50 % of an inactive carbon causes enhancement of radiocarbon age of about 5700 years (one half-life of ^{14}C) without respect to the real age of a sample.

The condition of trustworthy results is sampling of water from such boreholes, in which inflows are isolated from their overlying and/or underlying strata. All pipes of each borehole are cemented above perforation. So it is technically prevented from inflows of waters into the borehole from its sealed part. This way, however, cannot prevent from mixing of waters during their flow in aquifers. Such cases can occur especially in discharge areas of MTW. Then the waters of deep flow may be influenced by shallow ground waters or by precipitation.

These are the cases of boreholes BJ-101 in Lúčky (No. 22), Izabela in Vyšné Ružbachy (No. 29), BR-3 in Bojnice (No. 43), B-6 and B-15 in Santovka (No. 2), Kúpelný and GA/1A in Gánovce (No. 13) and BB-1 and BB-2 in Slatina (No. 23). We also sampled neighbouring boreholes in the same hydrogeological structure for comparison. Long-term experience has shown that ascending ways (faults) of MTW practically represent "sealed pipes" so that mixing of waters does not take place. However, geologic position of boreholes can influence considerably the results of isotope analyses, as mentioned in the following text.

Boreholes BJ-101 in Lúčky (No. 22) and HGL-2 in Kalameny (No. 33) are in the same hydrogeological structure. If water from borehole BJ-101 were influenced by the present-day precipitation, its age (23 ky) would be lower than the age of water (18.3 ky) from borehole HGL-2. Similarly, influencing would be reflected in the ^{18}O values. In water from borehole BJ-101 the ^{18}O value is 10.75 ‰ and from borehole HGL-2 the value is –11.25 ‰. Almost identical values are also for ^{13}C in bicarbonates and free CO_2 (for BJ-101 this is 0.81 ‰ and 7.27 ‰, and for HGL-2 it is 1.35 ‰ and 8.39 ‰, respectively).

Next we shall compare borehole BR-3 in Bojnice (No. 43) with borehole BR-1 at the same locality. According to different waters temperatures (for borehole BR-3 T = 34.5 °C and for borehole BR-1 T = 46.5 °C) the water from borehole BR-3 is influenced by waters with shallower circulation from present-day precipitation (O. Franko and J. Franko 2000). The apparent ^{14}C age of waters (9.1 and 8.7 ky) is, however, similar for both boreholes. Also, the ^{18}O and ^{13}C values are similar (for BR-3, ^{18}O = 10.03 ‰, ^{13}C = 7.12 ‰ and –14.11 ‰ and for BR-1, ^{18}O = 9.96 ‰, ^{13}C = 7.36 ‰ and –14.69 ‰, for bicarbonates and free CO_2, respectively).

Borehole B-3 in Malinovec (No. 5) catches water directly from the Triassic limestones and dolomites aquifer, while boreholes in Dudince (No. 3) are located in basal Neogene clastics. We know from hydrogeology of the area that, genetically, these are equal waters

(Melioris 2000). The waters in Dudince could be then influenced by own waters of aquifers. The apparent ^{14}C ages of waters (28 ky for B-3, 31 ky for HVD-2 and 28 ky for S-3) and the ^{18}O values are very similar (11.28 ‰ for B-3, 11.44 ‰ for HVD-2 and 11.27 ‰ for S-3). Similarly, the values of ^{13}C isotope are practically equal (+0.74 and –4.94 ‰ for B-3, +0.28 and –6.37 ‰ for HVD-2, and 0.05 ‰ and –6.61 ‰ for S-3).

We know that mineral waters from Santovka (No. 2) and Slatina (No. 23) are mixed waters (Melioris 2000). Their basis are equal waters as in Malinovec and Dudince, however, they have been mixed with infiltrated recent waters accumulated in Neogene volcanoclastics and alluvial sediments. This is also indicated by the apparent ages of waters and ^{18}O values (10.19 ‰ for B-6 (the age is 31 ky), 10.15 for OB-15 (the age is 18 ky), 10.20 ‰ for BB-1 (the age is 22 ky), and 9.76 ‰ for BB-2 (the age is 9 ky). Also, the ^{13}C values are different (for No. 2, B-6, ^{13}C = 0.56 ‰ and –5.44 ‰, for B-15, ^{13}C = 2.84 ‰ and –8.19 ‰, for No. 23, BB-1, ^{13}C = 3.71 ‰ and –7.02 ‰, and for BB-2, ^{13}C = 7.17 ‰ and 11.08 ‰), as listed in Tables 1 and 2.

Boreholes ŠHB-2 and BC-1 in Brusno (No. 4) intercept waters in various hydrogeological structures, although they are at distance of 100 150 m from each other. To this difference, the various ages of waters correspond (for ŠHB-2 the age is 16.3 ky, and 20.1 ky for BC-3), and the ^{18}O values are similar (10.08 ‰ for ŠHB-2 and 10.17 ‰ for BC-3). These differences are also manifested by different ^{13}C values (7.81 ‰ and –12.36 ‰ for ŠHB-2, and 4.46 ‰ and –10.60 ‰ for BC-1).

Thermal waters in Gánovce (No. 13) are caught by shallow boreholes. In the same hydrogeological structure the same waters are caught by deep boreholes in Vrbovo (No. 11). Waters in Gánovce are not influenced by shallow waters, because they are practically of the same age (26.9 and 25.2 ky) and have the same ^{18}O values (11.21 ‰ and 11.23 ‰, respectively) as waters in Vrbovo (27.1 and 26.1 ky, and ^{18}O = 11.36 and –11.50 ‰, respectively). Similarly, the ^{13}C values are equal (for No. 13, Kúpelný, ^{13}C = 0.21 ‰ and –6.56 ‰, for GA/1A, ^{13}C = 0.63 ‰ and –6.01 ‰, for No. 11, VR-2, ^{13}C = +0.92 ‰ and –6.24 ‰, and for VR-1, ^{13}C = +1.38 ‰ and –5.98 ‰).

4. Discussion

With regards to the contamination of some waters by the stable carbon (CO_2 of mantle origin) it is possible to compare ages of waters only from such localities where ^{13}C values in waters are comparable. For example, in Turčianske Teplice waters from boreholes TJ-20, TTS-1 and TJ-3 have approximately the same ^{13}C values, but e.g. in Santovka, water from the borehole B-6 the ^{13}C values (0.56 and 5.44 ‰) are higher than water from the borehole B-15 (2.84 and – 8.19 ‰). The ^{13}C values in water from the borehole B-6 point on the contamination by stable carbon, therefore the real age of this water will be lower than that given in Table 2.

The calculated radiocarbon apparent ages of waters varied within 32 ky and 9 ky (Table 2). This might give an idea on te he time intervals of MTW flow from their recharge areas to their present-day outflows. Relation between the infiltration time of precipitation, from which MTW originated, and climatic changes during the Würm is in Fig. 5. Climatic changes are represented by oscillation of the snow line in the Tatra Mts. (Lukniš 1964). The particular Würm periods are correlated with its period in Central Europe and the course of the snow line with glaciation in the Alps and the Northern Europe. From the view of individual Würm periods, three facts are visible from the snow line. First, the Paudorf period does not coincide completely with the Würm 2 3 period. Second, the small Bölling and Alleröd periods are insignificant, because they fall unambiguously in permanent withdrawal of the snow line. Third, we cannot consider the altitude of the snow line 1700 m a. s. l. as absolute   17 issues of MTW are close below it. These issues and/or localities of MTW have infiltration areas in altitudes lower than 1700 m a. s. l. at present (an exception is the locality Vyšné Ružbachy, No. 24). As for the last Würm stadial it is necessary to mention that not only this, but all the Würm glaciation was found in the Tatra and Low Tatra Mts. only. According to the differences between considerable glaciation of the Low Tatra Mts. northern slopes and insignificant traces of their southern slopes, the ridge of these mountains was a significant climatic boundary during the last glacial. Then outside the territory of the Tatra and Low Tatra Mts. northern slopes precipitation infiltrated in the remaining territory of Slovakia. In this period the January isotherms with values about –16 to –18 C and July isotherm with values 11 12 C took their course through the territory of Slovakia (Klute 1951).

In principle, it is valid that older waters of atmospheric origin are lighter and/or have lighter oxygen (Fig. 6). The ^{18}O values of present-day precipitation on the territory of Slovakia are varying within the limits of –8.70 ‰ to –10.44 ‰ in average (for the years 1988 1997) (Michalko 1999). In lowlands, ^{18}O varies from –8.70 ‰ to –9.45 ‰, and in the mountains between –10.10 ‰ and –10.44 ‰. The altitude of lowlands varies within the limits of 113 345 m a. s. l., and of the mountains within the limits of 692 2008 m a. s. l. When tracing springs in the Velká Fatra Mts. from carbonates of the envelope unit and the lower (Krížna) nappe, it has been established that with higher altitude the ^{18}O value is sinking by 0.1 ‰ to 100 m (Michalko and Malik 1998). With regard to the infiltration areas, we may take into consideration the values from the mountains and we know that their altitude in the Würm was lower from the present-day one. So, for instance, the Tatra raised by about 300 400 m during the late Pliocene and Pleistocene (Lukniš 1959). In spite of that, most of MTW have ^{18}O lighter than present-day values of precipitation in the mountains. Fig. 6 confirms the previously mentioned relations. The oldest waters (23 32 ky), which infiltrated in the Paudorf (melting of snow and glaciers) have the lightest oxygen (from 10.75 ‰ to –11.83 ‰) and vice versa. This regularity (there are also exceptions) is obvious from Fig. 6.

5. Conclusions

Several observations have been made in this paper which could be summarized as follows:

- The first MTW started to outflow by the end of the Upper Pliocene, 2 My ago, as evidenced by the oldest travertine occurrences.
- Next MTW outflowed during the interglacial (Günz-Mindel, Mindel-Riss, Riss-Würm) and interstadial periods (Günz 1 2, Würm 1 2) 900 70 ky ago, after the geologic and relative age of travertine deposits.

- In general the number of outflows of MTW increases with the younger age of interglacials.
- Radiocarbon apparent ages of MTW ranged between 32 ky and 9 ky, thus indicating the approximate time interval between the MTW recharge and their present-day out-flows from wells.
- MTW which are outflowing at present were infiltrated during the interstadials Würm 2 3, Würm 3 and the Holocene.
- The ^{18}O values of MTW are varying from –9.89 ‰ to –11.83 ‰, however, in the oldest waters (23 32 ky) the interval is between –10.75 ‰ and –11.83 ‰. The oldest waters infiltrated in the Paudorf (melting of snow and ice). Younger waters with heavier oxygen content infiltrated later.
- In the Holocene MTW continue to outflow at all the investigated localities, or in their vicinity.

Acknowledgements

We are grateful to the owners of wells for making us possible to take water samples for isotopic analyses. We also thank our colleagues for their assistance in collecting and treatment of water samples in the field and in laboratories.

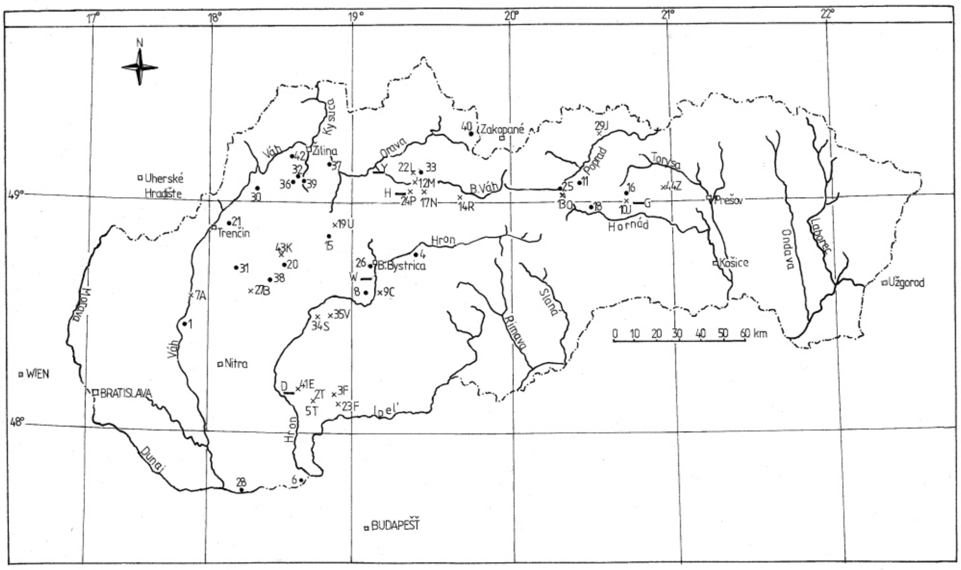

Fig. 1. Location map of mineral and thermal waters and deposits of travertines in Slovakia.

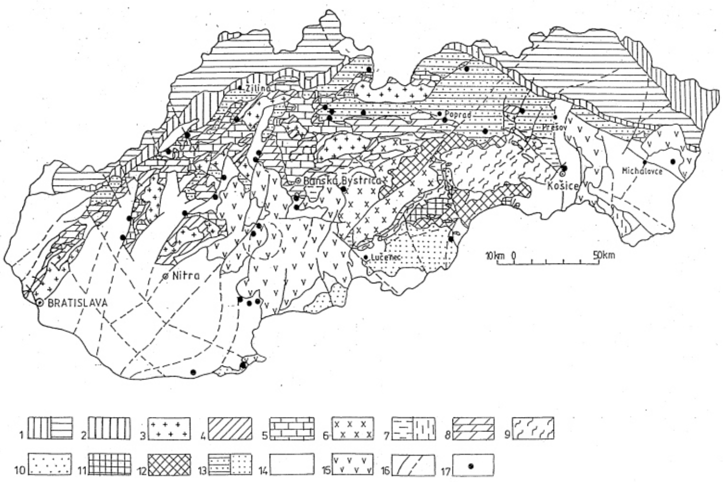

Fig. 2. Geothermal springs of Slovakia (O. Franko, 1999. Tectonic sketch J. Vozár and Š. Káčer Eds., 1998). 1 Outer Flysh belt; Krosno zone, Magura zone; 2 Klippen belt; 3 Tatricum basement; 4 Tatricum cover unit; 5 Fatricum; 6 Veporicum basement; 7 Veporicum and Zemplinicum cover unit; 8 Hronicum; 9 Gemericum; 10 Meliaticum; 11 Turnaicum; 12 Silicicum; 13 Inner Carpathian Paleogene, Buda basin; 14 Neogene basins; 15 Neogene volcanics; 16 main faults; 17 Springs.

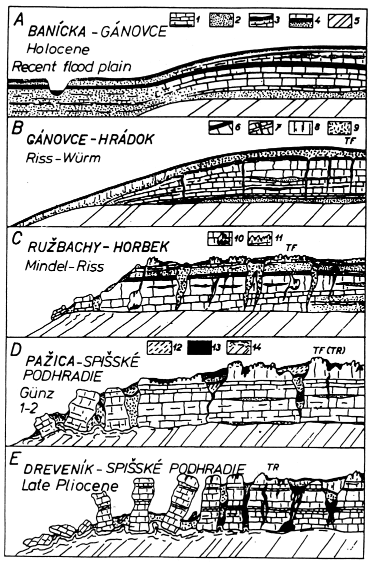

Fig. 3. Relative age of travertines according to their disintegration (V. Ložek, 1973,completed by O. Franko, 1999). Travertines: A youngest, B young, C old, D older, E oldest. 1 Solid travertines, 2 loose tufas, 3 surficial rendzimas, 4 buried rendzimas, 5 substatum of travertines, 6 frost disturbing of solid travertines surface, 7 joints in travertines, 8 loess, 9 loamystone scree, 10 small caves with sinter decoration, 11 karren, 12 layers of loess in holes, 13 erras (TF terra fusca, TR terra rossa), 14 pressuredeformed substratum.

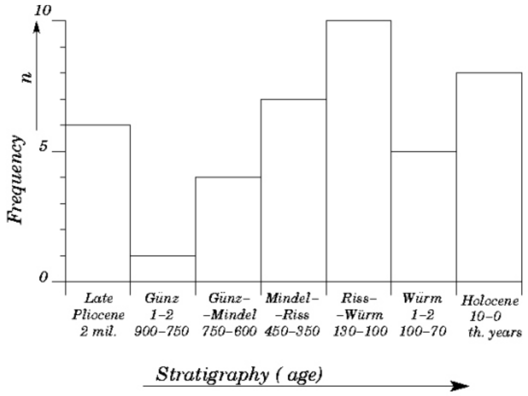

Fig. 4. Histogram of travertine deposit distribution.

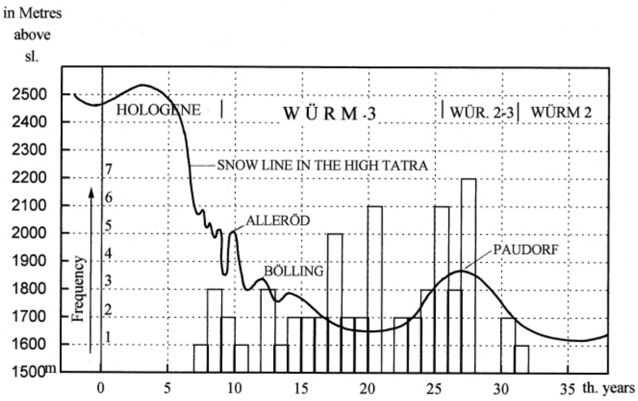

Fig. 5. Correlation of radiocarbon age distribution of the MTW according to ^{14}C isotope and snow line.

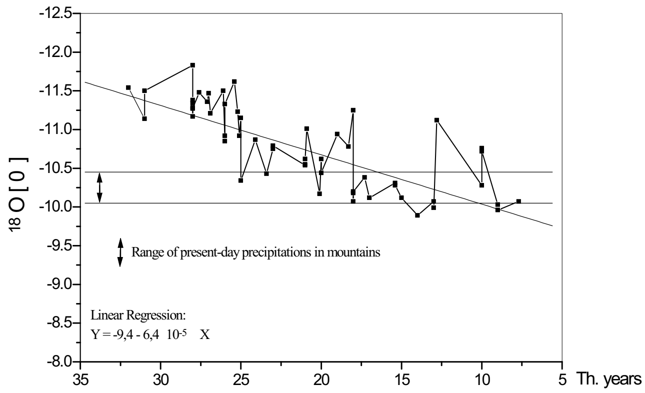

Fig. 6. Correlation of the thermal water age according to the ^{14}C isotope and ‰

Table 1. Description of the wells.

No.	Locality	Well	Aquifer 1 Stratigraphy	Water temperature (^{o}C)
1	Koplotovce	KB – 2 KB – 2	L, D T	22.2 20.0
2	Santovka	B – 6 B – 15	V, L, D S, T	14.5 14.1
3	Dudince	HVD – 2 S – 3	V, G, Sd. B, T	22.5 26.9
4	Brusno	ŠHB – 2 BC - 1	L, D T	24.0 19.8
5	Malinovec	B – 3	L, D T	26.0
6	Štúrovo	FGŠ – 1	L, D T	38.4
7	Pieštany	V – 8 V – 4A	"	60.2 61.9
8	Kováčová	K – 2	"	47.9
9	Sliač	Ia	"	32.4
10	Sivá Brada	B – 2	"	15.4
11	Vrbov	VR – 2 VR – 1	"	57.9 54.2
12	Bešenová	ZGL – 1	"	60.1
13	Gánovce	Kúpeľný GA – 1/A	"	23.3 25.6
14	Liptovský Ján	Rudolf	"	28.8
15	Turčianske Teplice	TJ –20 TTŠ – 1 TJ – 3	"	45.1 43.6 42.3
16	Lúčka	B Š – 1	"	29.0
17	Vyšný Sliač	Čertovica	"	9.1
18	Arnútovce	HKJ – 3	"	30.5
19	Mošovce	HV – 63	"	20.1
20	Laskár	Š1 – NBII	"	66.5 66.7
21	Trenčianske Teplice	P – 1 SB – 5 V – 3	"	38.8 40.5 41.4
22	Lúčky	BJ – 101	"	32.2
23	Slatina	BB – 1 BB – 2	C, Q N, T	16.8 15.3

Table 1. Description of the wells (*continued*).

No.	Locality	Well	Aquifer 1 Stratigraphy	Water temperature (°C)
24	Lipt. Štiavnica	LŠH – 1	L, D T	19.3
25	Poprad	PP – 1	"	44.5
26	Ban. Bystrica	BB – 1	"	20.7
27	Malé Bielice Velké Bielice	MB – 3 VB – 2	C, L, D N, T	39.3 38.8
28	Patince	SB – 2	L, D Ls, T	26.0
29	Vyš. Ružbachy	Izabela	L, D T	20.3
30	Belušské Slatiny	Kúpeľný BS – 2	"	18.1 18.9
31	Bánovce n/B	BNB – 1	"	41.8
32	Rajecké Teplice	BJ – 19	"	37.3
33	Kalameny	HGL – 2	"	33.5
34	Vyhne	H – 1	"	33.9
35	Sklené Teplice	ST – 1 ST – 2	"	51.3 51.5
36	Rajec	RK – 22	C Pg	25.4
37	Stráňavy	ŽK – 2	C, L, D Pg, T	21.5
38	Chalmová	HCH – 1	L, D T	40.8
39	Kamenná Poruba	RTŠ – 1	C, L, D Pg + T	41.1
40	Oravice	OZ – 2 OZ – 1	L, D T	41.6 21.0
41	Kalinčiakovo	HBV – 1 HBV – 2A	L T	25.2 25.0
42	Peklina	ŽK – 5	C Pg	13.7
43	Bojnice	BR – 1 BR – 3	L, D / T Sd, L, D / Pg, T	46.5 34.5

[1]L Limestones, D Dolomites, V Vulcanoclastics, G Gravels, Sd Sandstones, C Conglomerates, Q Quartzites, T Triassic, S Sarmation, B Badenian, N Neogene, Ls Lias, Pg Paleogene.

Table 2. Radiocarbon age and ^{13}C and ^{18}O isotopes.

No.	T.D.S. (g L ^{1})	^{13}C HCO_3 ‰)	^{13}C CO_2 (‰)	Age (Years)	^{18}O H_2O (‰)
1	2.88 2.55	4.44 4.52	9.14 8.98	32000 2000 31000±900	11.54 11.50
2	3.81 3.35	0.56 2.84	5.44 8.19	31000±3300 18000±300	10.19 10.15
3	6.91 6.00	+0.28 0.05	6.37 6.61	31000±1050 28000±730	11.14 11.27
4	1.31 2.50	7.81 4.46	12.36 10.60	16300±180 20100±280	10.08 10.17
5	6.25	+0.74	4.94	28000±730	11.28
6	0.75	7.61	15.02	28000±700	11.17
7	1.28 1.36	7.95 8.66	 11.55	28000±740 26000±560	11.34 11.33
8	2.75	3.94	8.55	28000±740	11.38
9	3.82	2.32	6.76	28000±710	11.83
10	7.64	+3.44	3.35	27600±720	11.48
11	4.00 3.99	+0.92 +1.38	6.24 5.98	27100±790 26100±700	11.36 11.50
12	2.98	1.20	6.49	27000±750	10.47
13	3.69 3.71	0.21 0.63	6.56 6.01	26900±650 25200±520	11.21 11.23
14	3.95	+1.03	6.03	26000±710	10.85
15	1.50 1.65 1.50	2.33 2.87 2.20	8.38 8.50 8.02	26000±580 25100±520 23100±490	10.85 10.72
16	6.02	+0.87	5.00	25400±540	11.62
17	3.05	0.85	6.54	25000±630	10.34
18	1.52	4.08	10.08	25000±520	11.15
19	1.48	1.80	8.20	24100±550	10.87
20	0.97 0.97	4.32 5.43	16.71 11.68	23400±430 21000±400	10.43 10.54
21	2.83 2.72 2.72	6.26 7.52 8.79	11.65 10.05 9.40	23000±500 21000±400 20000±340	10.79 10.62 10.62

Table 2. Radiocarbon age and ^{13}C and ^{18}O isotopes (*continued*).

No.	T.D.S. (g L ^{1})	^{13}C HCO_3 ‰)	^{13}C CO_2 (‰)	Age (Years)	^{18}O H_2O (‰)
22	2.88	0.81	7.27	23000 490	10.75
23	3.59 1.35	3.71 7.17	7.02 11.08	22000 480 9000 98	10.20 9.76
24	3.48	0.72	6.47	21000 320	10.55
25	3.08	1.21	6.96	20900 380	11.01
26	3.30	2.94	7.87	20100 320	10.17
27	1.07 0.85	3.52 6.62	10.23 12.98	20000 280 15000 230	10.44 10.12
28	0.72	9.00	16.09	19200 260	10.94
29	1.68	2.96	7.99	18300 230	10.78
30	1.82 1.78	5.62 4.71	9.09 9.68	16700 190 16400 180	10.20 10.12
31	0.57	8.81	12.02	18300 280	10.07
32	0.68	4.85	12.62	17700 260	10.18
33	2.61	1.35	8.39	18300 280	11.25
34	1.19	3.92	9.44	17300 200	10.38
35	2.52 2.52	6.77 6.53	12.88 11.95	15400 190 15400 160	10.28 10.31
36	0.49	6.14	17.40	15400 160	10.12
37	0.42	8.50	16.66	14400 170	9.89
38	1.37	4.26	13.12	12700 200	9.99
39	0.39	8.26	16.22	13000 150	10.07
40	1.27 0.89	9.14 12.66	16.36 20.70	12800 170 7700 90	11.12
41	1.03 1.03	9.15 9.54	14.34 8.55	9900 100 9600 100	10.72 10.76
42	0.58	8.06	20.98	10100 90	10.28
43	0.70 0.68	7.12 7.36	14.11 14.69	9100 140 8700 110	9.96 10.03

Numbering as in Table 1.

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