# Isotope Hydrology of the Artesian Aquifers of the Styrian Basin, Austria

A progress Report

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#### Introduction

The Austrian part of the Styrian Basin occupies about 6000 km<sup>2</sup> in Styria and Burgenland on the southern flanks of the eastern Alps. The basin is bordered on the west and northwest by crystalline rocks of the Central Zone of the Alps, and extends eastward into Yugoslavia and Hungary. The rocks of the Alpine Central Zone are overlain in the basin by up to 3000 m of poorly consolidated Tertiary sediments, marine at the base and grading upward into non-marine deposits with a thin mantle of deposits of Quarternary age. These Tertiary deposits, which dip generally eastward, contain layers and lenses of sand and gravel that yield water readily to wells. Throughout most of the basin the uppermost Pliocene deposits (Pannonian) are fine grained and confine water in underlying sands of Sarmatian age. Locally, confined water is also found in permeable zones in the Pannonian and local confinement has even been observed in Pleistocene deposits.

The relief in the Styrian Basin is much less than in the nearby mountains, but nonetheless, the Tertiary fill of the basin has been carved into a rugged local relief by the streams draining the Alps. This local relief is of the order of 100 to 150 meters from valley floor to ridgetops. Wells drilled in the valley bottoms into the confined aquifers generally flow. Some 1000 such wells have been drilled over the past century to provide domestic, stock, and small industrial and municipal water supplies. Draft on the artesian system has increased substantially in the past two decades and decline in artesian head has been noted in several areas.

Due to local concern over the decline in artesian head the Vereinigung für hydrogeologische Forschung in Graz is carrying out a comprehensive study of the ground waters of the basin, and this has been designated as a representative basin study within the Austrian programme for the International Hydrological Decade. The IAEA has been collaborating with Doz. Dr. J. ZOETL of the VHFG in making isotopic studies of the ground waters, which form the subject of this report. The views expressed in the paper are those of the authors and do not necessarily represent the views of the IAEA.

#### Purpose and Scope of the Investigation

The hydrologic evidence available at the beginning of the investigation indicated that under natural conditions ground water in the artesian system was moving, perhaps very slowly, from recharge areas where the aquifers are exposed along the western border of the basin generally eastward in accordance with the general slope of the land surface. Also, although it was known that more than one confined system existed in certain areas, it was not clear how extensive such separation of water bodies was. The purpose of the isotope studies was to (1) characterize the waters of separate aquifer systems, (2) to determine whether active circulation exists in the artesian systems, and (3) if feasible, to calculate the velocity of ground water flow from determinations of the time of recharge at different points in a single system.

A brief reconnaissance sampling was carried out in August 1966 in which 8 flowing artesian wells distributed over a wide area were sampled for analysis for tritium (<sup>8</sup>H), deuterium (<sup>2</sup>H), oxygen-18 and carbon-14. The sampling points are shown on figure 1 and the results are presented in table 1 (Str 1-8). The analyses indicated a wide range in the content of stable isotopes (<sup>2</sup>H, <sup>18</sup>O), which was quite encouraging for the further use of these isotopes in the investigation. They showed also that the tritium content was in most cases not significantly above zero, suggesting recharge longer than 40 to 50 years ago. The analyses for <sup>14</sup>C indicated time of recharge on the order of several thousand years for most of the waters sampled. It should be noted at this point that the apparent age calculated from the raw <sup>14</sup>C data is only relative and is subject to large reduction due to dilution of the radioactive carbon present in ground waters by carbon dissolved from minerals in the rocks. To make a proper correction for this effect requires analysis of the <sup>13</sup>C content of the waters, which is still in progress.

On the basis of these preliminary results it was decided to concentrate additional sampling in 1967 in two areas, where the conventional hydrologic investigations of the VHFG were far advanced, and the relations of the several aquifers were better known than in the rest of the basin. These areas, Hartberg—Grafendorf and Prebensdorf—Altenmarkt, are shown in figure 1 and the analyses available at the time of writing are presented in table 1 (Grz 1—25) together with pertinent well data. All samples are being analysed for deuterium, <sup>18</sup>O, and most

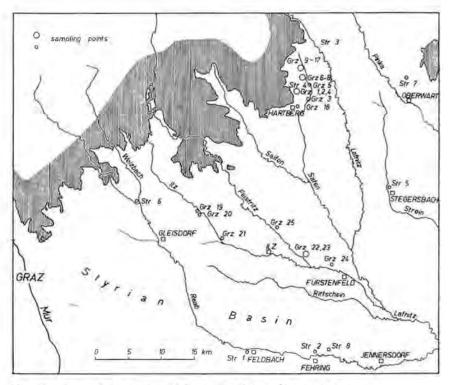


Fig. 1: General features and location of sampling points.

for tritium. On the basis of these results a selection has been made of samples to be analysed for <sup>14</sup>C. In general, sources that contain substantial amounts of modern recharge as indicated by tritium content are not analysed for <sup>14</sup>C.

# **Isotope Relations**

The environmental isotopes used widely in hydrologic work include the heavy stable isotopes of water, deuterium and <sup>18</sup>O, and the radioactive isotopes tritium and <sup>14</sup>C (found in the dissolved carbon species present in all natural waters). The stable isotopes occur in natural waters in average concentrations of about 160 parts per million in the case of deuterium, and about 2000 ppm in the case of <sup>18</sup>O. Small but significant variations occur in the stable isotope contents of natural waters, which can be measured with great precision by mass spectrometry.

# Table 1

Sampi No,	e Location/Owne <del>r</del>	Sampling Date (Mo/Yr)	Well Depth (M)	Casing Depth (M)		
Str	Feldbach/Mahr	8-66	92	92	1880	
	2 Johnsdorf/Kainz	8-66	88	88	1936	
12	Neustift/Koller	8-66	86	85	1955	
	Penzendorf/Fischer (Grz 1)	8-66	119	24	1952-	
	Stegersbach/Fenz	8-66	116	116	1956	
	5 St. Ruprecht/Rosenberger	8-66	70	55	1950	
	Unterschützen/Portschy	8-66	279	12		
	Weinberg/Siegl	8-66	55	30	1939	
Grz	Penzendorf/Fischer (Str 4)	6-67	119	24	1952-	
3	Penzendorf/Molkerei	6-67	150	105	1966	
	B Eggendorf/Zettl	6-67	78	48	1936	
	Penzendorf/Lechner	6-67	116	103	1935	
13	Untersafen/Schlögel	6-67	170	100	1953	
- 3	Obersafen/Tittinger	6-67	75	25	1930	
13	Obersafen/Teubel	6-67	33		1953	
	B Obersafen/Fink	6-67	101		1940	
1	Grafendorf/Fuchs	7-67	70			
1	) Grafendorf/Kogler	7-67	80	80	±1949	
1	Grafendorf/Ritter	7-67	136	54?	$\pm 1949$	
1	2 Grafendorf/Kundegraber	7-67	70			
1	Seibersdorf/Koller	7-67	36	26	1926	
1	Grafendorf/Ringhofer	7-67	69		$\pm 1949$	
1	i Seibersdorf/Maierhofer	7 - 67	64			
1	Grafendorf/Kappler	7-67	26	25?	$\pm 1949$	
1	Grafendorf/Rechberger	7-67	49		$\pm 1949$	
1	B Hartberg/Molkerei	7 - 67	192	192	1965	
1	Prebensdorf/Maisinger	11-67	136	80	1958	
	) Prebensdorf/Kochauf	11 - 67	60	12-18	1956	
2	Sinabelkirchen/Pratscher	11-67	187		1930	
2	Grosswilfersdorf/Molk. 144	11-67	144	144	1950	
2	Grosswilfersdorf/Molk. 104	11-67	104	104	1929	
	Altenmarkt/Fabian	11-67	28-30	12	1928	
	5 Hainersdorf/Damm	11-67	64	ca.	1918	

Isotope analyses and pertinent well records for samples

of artesian waters of the Styrian Basin

	Discharge	Deute-	Oxygen	Carbon —14	Apparent Age <sup>2</sup>		ritium
Tempera- ture (°C)	(litres/ sec)	rium <sup>1</sup> ð ‰	$-18^{1}$ 8 %	(% Modern			r. u.)
13.4	0.016	-68.2	- 9.61	35.3 ±1.6	8364	0.3	±0.3
13.8	0.200	-69.1	-10.31	$23.2 \pm 0.7$	11736	0.5	±0.:
	1.000	-75.9	-10.27	$1.96 \pm 0.9$	31425	0.9	±0.8
15.3	0.102	-60.4	- 8.83	$30.5 \pm 1.5$	9538		)±0.3
12.4	0.250	-75.6	-10.96	$10.9 \pm 0.7$	17840	0.4	±0.:
		-66.7	- 9.83	$28.2 \pm 1.2$	10168	0.6	±0.8
24.9	0.370	-69.8	-10.53	$1.66 \pm 0.8$	32730	0	±0.4
12.1	0.129	-63.9	- 9.52	55.8 ±1.7	4543	1.3	±0.8
15.3	0.047	-60.1	- 8.90	$23.7 \pm 0.7$		0.4	±0.5
13.2?	6.000	-62.9	- 8.93	$33.8 \pm 1.0$	8713	0.1	±0.:
12.7?	0.168	-61.0	- 8.42	31.0 ±0.6	9408	0.6	±0.5
13.2			- 8.85			0	±0.5
14.1		-58.3	- 8.15	$40.0 \pm 1.2$	7360	1.4	±0.3
13.8	0.125		- 7.96			0.7	±0.3
		-70.3	- 9.00			1.0	±0.4
		-64.5	- 8.52	25.5 ± 0.8	10976	0.9	± 0.4
12.6	0.103	-61.7	- 8.53	29.5 ±1.2	9806	1.1	±0.:
14.0	0.225	-57.0	- 8.61			1.1	±0.4
13.9	0.143	-62.9	- 8.09	38.7 ±0.8	7625	1.2	±0.3
12.3	0.091	-61.3	- 8.45			3.3	±0.:
12.1	0.038	-64.2	- 8.19	$32.2 \pm 1.0$	9102	0.9	±0.3
13.5	0.033	-61.7	- 8.50	$36.9 \pm 1.0$		1.1	±0.3
13.8		-65.4	- 8.27			1.4	±0.5
12.3	0.015	-59.2	- 8.49			6.3	±0.0
12.4	0.023		- 8.69			0.2	±0.4
17.5	5.000	-70.3	- 9.55	$2.4 \pm 0.5$	29960	0.1	±0.4
12.7	0.220						
10.9	0.040						
16.5	0.110						
16.0	0.080						
	0.200						

 $^1$  As reportet by laboratory, precision is  $\pm\,2\%$  for deuterium,  $\pm\,0.2\%$  for  $^{18}0.$ 

<sup>2</sup> Not corrected for dilution by non-radiogenic mineral carbonate, see p. 57.

Tritium and <sup>14</sup>C are produced by cosmic-ray bombardment of the upper atmosphere. These radioactive isotopes decay exponentially with half-lives of 12.26 and 5568 years, respectively. Since 1954 the natural input has been engulfed by injections of tritium and <sup>14</sup>C stemming from atmospheric testing of thermonuclear weapons, which have occurred at variable rates. Since 1960 the tritium, deuterium and <sup>18</sup>O contents of precipitation have been monitored on a world-wide basis (IAEA, 1967); the nearest station in this world network to the Styrian Basin is at Vienna.

The spatial and time variability of input of the four environmental isotopes in the hydrologic cycle, and the decay of the radioactive isotopes are the key to their interpretation in hydrologic investigations. The trends of tritium and the stable isotopes in precipitation are now fairly well known and with data from world network stations, input for given areas can be estimated with reasonable precision, thus providing a starting point for local hydrologic interpretation of isotopic data.

The special value of the stable isotopes in hydrologic studies stems from the fact that whenever water changes state as by condensation, evaporation, or freezing an isotope fractionation occurs and the heavy isotopes tend to be enriched in the phase having lower vapour pressure. This effect is governed mainly by temperature of evaporation and condensation; the lower the temperature the greater is the depletion in stable isotopes. Thus, in Austria a marked seasonal variation is observed in stable isotope content of precipitation corresponding to the seasonal temperature variations. Similarly, precipitation in the Eastern Alps is depleted in stable isotope content relative to that at Vienna owing to the orographic decrease in average temperature.

As hydrologic phenomena tend to smooth the variability of input, streams show less variability than precipitation, and ground waters show little or no seasonal variability in their input; generally their stable isotope content agrees closely with long-term weighted averages of that of the precipitation during the recharge seasons.

The special value of tritium and <sup>14</sup>C in hydrologic studies is due to their property of radioactive decay, which can be used to date the time of recharge to a ground water. Once removed from contact with the atmosphere these radioactive isotopes in ground water are not replenished and they decay at a known, consistent rate. Owing to its short half-life of 12.26 years, the presence of measureable amounts of tritium is unequivocal evidence of a component of modern recharge in the water. If the tritium content is above that accountable as due to the natural pre-thermonuclear level of precipitation (about 10 T. U. in Austria), then this is evidence of some post—1954 recharge.

<sup>14</sup>C with its long half-life of 5568 years is of special value in dating recharge of slow moving ground waters in artesian systems. Unlike

hydrogen and oxygen which form part of the water molecule, carbon occurs in dissolved form and may be added to or removed from a water in transit. This greatly complicates the precise dating of recharge by <sup>14</sup>C, as a rather detailed knowledge of the carbonate chemistry of the system is required to interpret the <sup>14</sup>C data properly. Nontheless, even the relative ages indicated by uncorrected <sup>14</sup>C results can be of great value in determining the history of a given water.

# Sampling and Analysis

Sampling for tritium, deuterium and <sup>18</sup>O is simply a matter of filling a polyethylene sample bottle, capping it and sending it to the laboratory. The quantity of water required is 500 ml for tritium and 20 ml for both deuterium and <sup>18</sup>O.

Sampling for <sup>14</sup>C is a little more complicated. In order to provide sufficient carbon for reasonable measurement precision a sample of 100 liters of water is required of waters of the general range of carbonate content of the ground waters of the Styrian Basin. It can be seen that transport of such large volumes of water even over short distances would be awkward; therefore, a procedure is followed in the field for precipitating the carbonate species present in the water, and this precipitate is then forwarded to the laboratory. In this technique 100 liters of water is placed in a large metal funnel to the bottom of which a sample bottle is screwed. NaOH is added to the sample to convert all the dissolved carbonate species present to carbonate ion CO<sub>3</sub>, FeSO<sub>4</sub> is added to facilitate rapid settlement of precipitate, and BaCl<sub>2</sub> is added to convert the dissolved carbonate present to insoluble BaCO<sub>3</sub>, the funnel is capped with a plastic lid and the precipitate settles in the sampling bottle at the bottom of the cone about three hours. The sample, contained in a 1-liter bottle, is then shipped to the laboratory.

The analyses of the isotopic content of the waters are done by standard methods, which therefore will not be described in detail here.

Deuterium and <sup>18</sup>O were analyzed by mass spectrometry by Prof. W. DANSGAARD at the University of Copenhagen. The results for both stable isotopes are expressed in deviation (3) per mil (‰) from a standard mean ocean water, SMOW (H. CRAIG, 1961). In routine analyses the precision is about 2‰ for deuterium and 0.2‰ for <sup>18</sup>O.

Tritium and <sup>14</sup>C were analyzed by gas counting in the laboratory of IAEA in Vienna. Tritium is first enriched by electrolysis, then is converted into the form of ethane and the radioactivity of the ethane is measured in a gas proportional counting system (J. F. CAMERON & B. R. PAYNE, 1965). In the analysis for <sup>14</sup>C, the precipitate received from the field is treated with acid to release the CO<sub>2</sub> from the carbonate precipitate. The CO<sub>2</sub> is hydrogenated with hydrogen gas to produce methane (CH4) which is introduced into a gas proportional counter and the <sup>14</sup>C content is determined as a function of the radioactivity of the methane gas in comparison to a standard.

Tritium is reported as tritium units (T. U.), where 1 T. U. represents a concentration of 1 atom of <sup>8</sup>H in 10<sup>18</sup> atoms of <sup>1</sup>H. In routine analyses the precision is  $\pm 5$ —10<sup>0</sup>/<sub>0</sub> of the value reported. <sup>14</sup>C is reported as percentage of <sup>14</sup>C relative to a modern (pre-thermonuclear) standard (H. GODWIN, 1962). The precision is about  $\pm 10^{0}/_{0}$  of the stated value.

# Interpretation of Results Obtained

**Tritium** — The analyses of the samples taken in August 1966 ranged from 1 to 6 T. U. in tritium content; however, it was found later that these samples had been contaminated through storage in a room having a high tritium level in the ambient air moisture. Accordingly, these same sources were resampled in May, 1967 with the results shown in table 1. All these samples can confidently be considered dead in tritium except that of Weinberg/Siegl (STM 8), which is on the borderline of measuring significance ( $1.3 \pm 0.8$  T. U.). In view of the fact that this sample had the highest <sup>14</sup>C content of any sample from the Styrian Basin, this tritium measurement may well be realistic. It seems reasonable to conclude on the basis of tritium content alone that the other waters all exceed 40 years since recharge.

Samples Grz 1—18, collected in June and July 1967, ranged in tritium content from unmeasurable to 6.3 T. U. (table 1). The samples containing less than 1 T. U. are considered to be dead in tritium, while those exceeding 1.5 T. U. presumably contain at least a small component of modern water. The samples containing 1 to 1.5 T. U. are on the borderline of measuring significance and may or may not contain a modern component of recharge. Further study would be required to resolve this question with respect to the samples in this range.

**Carbon-14** — The analyses of samples collected in 1966 show a range in <sup>14</sup>C content from 1.66 to 55.8% of modern standard. Even allowing for very large corrections the samples containing 1 to 2% <sup>14</sup>C probably are of the order of 20,000 years since recharge. The samples from Weinberg/Siegl and Feldbach/Mohr, containing 55.8 and 35.3% of modern <sup>14</sup>C, respectively, may eventually prove to contain modern water after correction. This latter statement is quite tentative and is subject to revision on the basis of <sup>13</sup>C analyses still to be completed.

The results of analyses of samples collected in 1967 available at the time of writing range generally between about 30 and 40% of modern <sup>14</sup>C. With the exception of the sample from Hartberg/Molkerei, which contained 2.4% <sup>14</sup>C, all the samples analysed so far were from the vicinity Penzendorf—Grafendorf. Despite considerable differences in depths of wells there is a rather small variation in <sup>14</sup>C content, and as

noted previously little variation in tritium. These two lines of evidence together with the stable isotope data, which also shows little variation among these wells, suggests a generally homogeneous water with little stratification. The sample from Hartberg/Molkerei is of special interest because of its great apparent age, despite the fact that the well is near the margin of the sedimentary basin, and is in fact within 1 km of the contact of Tertiary sediments with crystalline rocks of the Alpine Central Zone.

Stable Isotopes — The wide variation of stable isotope content (fig. 2) of the samples collected in 1966 is considered highly significant especially in view of the wide variability in ages suggested by <sup>14</sup>C analysis of samples of the same waters. As the main supply of water to the Styrian Basin at present, and presumably in the Pleistocene as well, is from the Alps; the pronounced variability is tentatively interpreted as being due to general temperature changes during late Pleistocene and early Recent times. The magnitude of changes as reflected by range in <sup>18</sup>O content is consistent with values obtained by J. LABEYRE et al. (1967) from stalagmites from a cavern in France. Again confirmation of this concept will require additional <sup>13</sup>C data.

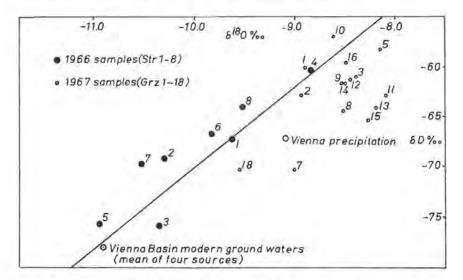


Fig. 2: Deuterium-oxygen-18 diagramme for artesian waters of the Styrian Basin. Trend line of D = 8 <sup>18</sup>O + 10 is characteristic of northern hemisphere continental precipitation. Shown for comparison are amount weighted average of precipitation at Vienna (1961–1965) and the average for four typical modern ground waters of the Vienna Basin.

Figure 2 is a deuterium—<sup>18</sup>O diagram showing ground water samples from the Styrian Basin. Also shown for comparison are the amount weighted average of stable isotope content of precipitation at Vienna (1961—1965) and the average for four typical modern ground waters from the Vienna Basin, on the opposite side of the Alps to the north. The trend line shown,  $\delta D = 8 \delta^{18}0 + 10$ , characterizes the average trend in Northern Hemisphere continental precipitation (W. DANSGARD, 1964). The rather wide range of stable isotope values in the 1966 samples has already been discussed in relation to <sup>14</sup>C content as being related to regional changes in temperature. The 1967 samples shown are relatively enriched in stable isotope content relative to the 1966 samples, but this is consistent with the fact that all but sample 18 (Hartberg/ Molkerei) are from the vicinity of Penzendorf and thus agree generally with the single sample from that area in the 1966 collection (Penzendorf/Fischer).

The pronounced depletion of the Vienna Basin ground waters relative to the Styrian Basin waters is believed due to a difference in average altitude of recharge areas. The principal recharge to the Vienna Basin ground waters is from the Schwarza River (G. M. Davis et al., 1967) which drains a higher altitude belt than the streams tributary to the Styrian Basin. As the average temperature decreases with altitude, greater depletion would be expected in the Vienna Basin ground waters.

The amount weighted stable isotope content of precipitation at Vienna, on the other hand is somewhat enriched relative to the 1966. Styrian Basin samples and the Vienna Basin ground waters. This is consistent with the hydrology of the area, as Vienna is at a lower altitude hence is warmer than either recharge area. Moreover the precipitation record includes the effect of rain during the warm summer months, which is minimized in the ground waters owing to consumption of rainfall by evapotranspiration which accounts for much of the potential recharge in the climate of Eastern Austria.

### **Preliminary Conclusions**

1. Reconnaissance sampling revealed pronounced variation in deuterium and <sup>18</sup>O content of artesian waters and suggested the utility of these isotopes for characterizing different ground waters.

2. Correlation of <sup>14</sup>C and stable isotope data suggests that differences in stable isotope content are related to time since recharge, and reflect climatic changes in late Pleistocene and Recent times. As more results accumulate this relations should be of value as a paleoclimatic indicator.

3. Low tritium content of most flowing wells and distribution of apparent age as indicated by <sup>14</sup>C content suggests little active circulation of ground water. No progressive increase in age away from outcrop areas was noted. Indeed, some of the lowest <sup>14</sup>C contents (oldest waters)

were from deep wells close to the basin margin, suggesting very sluggish circulation in the deep aquifers prior to development of the ground water resource by wells.

4. Detailed sampling of several depth zones in the Penzendorf— Grafendorf area suggests a fairly homogeneous water body with little vertical stratification in that area.

5. Much additional hydrogeologic and isotopic data will be required to resolve the ground water flow pattern before calculation of the velocity of ground water movement by <sup>14</sup>C dating will be practicable. The greatest need for isotope data is additional areal coverage and sampling with depth.

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#### Abstract

Analyses of waters from flowing wells in the Styrian Basin for tritium, carbon-14, deuterium, and oxygen-18 provide important clues re the rate of circulation of the artesian waters. Tritium levels generally less than 1 T. U. and <sup>14</sup>C contents generally less than 40% of modern indicate that circulation in the artesian system was very sluggish under natural conditions. A pronounced variability in deuterium and <sup>16</sup>C contents is ascribed to temperature variations in recharge waters in late Pleistocene and early Recent times.

# Résumé

La détermination des teneures en tritium, carbone-14, deuterium et oxygène-18 des échantillons prélevés dans des puits artésiens dans le bassin de Styrie donne des indications importantes sur la circulation des eaux souterraines dans les aquifères étudiées. Les teneurs en tritium qui sont en général an dessous d'une unité de tritium et les teneurs en <sup>14</sup>C qui sont inférieurs à 40% du carbone moderne montrent que la circulation dans le système artésiens est très lente dans des conditions naturelles. Les variations significatives en ce qui concerne les teneurs en deuterium et oxygène-18 dans la région étudiée sont attribuées à la variation des températures dans les eaux d'alimentation à la fin du pleistocene et au commencement de l'ère récente.

# Zusammenfassung

Analysen von Tritium, Carbon-14, Deuterium und Oxygen-18 von Wässern artesischer Brunnen des Steirischen Beckens sind ein wichtiger Schritt zur Erforschung des Haushaltes der gespannten Grundwässer dieses Bereiches.

Der Tritiumgehalt der bisher untersuchten Proben ist im allgemeinen kleiner als 1 T. U. und der Gehalt an Carbon-14 meist geringer als 40% rezenten Wassers, was auf eine sehr langsame Zirkulation der artesischen Wässer bei natürlichen Gegebenheiten hinweist. Die ausgesprochene Variabilität des Deuterium- und Oxygen-18-Gehaltes ist den Temperaturunterschieden der versickernden Wässer im späten Pleistozän und in der frühen Gegenwart zuzuschreiben.

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