USE OF ^{39}AR AND ^{14}C FOR GROUNDWATER DATING

HEINZ HUGO LOOSLI and HANS OESCHGER

Physics Institute, University of Bern
Sidlerstrasse 5, CH-3012 Bern, Switzerland

ABSTRACT. Cosmic-ray produced atmospheric ^{39}Ar activity (T$\frac{1}{2}$ = 269 yr) has been determined at 0.11 ± 0.012 dpm/lt argon. Ice samples from two profiles in Greenland bore holes showed conclusively that ^{39}Ar dating leads to correct ages. Corrections can be made for possible contamination of the samples with ambient air during field extraction and during laboratory processing by measuring ^{85}Kr in the same samples.

The following isotopes: ^{14}C, ^{39}Ar, ^{85}Kr, ^{3}H, partly ^{32}Si, ^{13}C, and ^{18}O were investigated in 20 groundwater samples. Unexpectedly large discrepancies between "^{14}C ages" and "^{39}Ar ages" were observed for many of these samples. For example, a horizontal profile of a confined sandstone aquifer in the Franconian Albvorland showed decreasing ^{39}Ar and ^{14}C activities from respectively, 100 percent to 17 percent and 80 percent to 0.3 percent of modern activity, corresponding to elapsed time periods of 700 and >20,000 years, respectively.

It seems unlikely that gas exchange through the aquiclude is the cause of this discrepancy. It can neither be explained by only assuming that the water represents a mixing of components with different ages. We detected the possibility of underground production of ^{39}Ar in thermal spring water from Zurzach, Switzerland. Its argon showed higher specific activity than atmospheric argon. Elsewhere, however, samples were found containing no detectable ^{39}Ar activity: two wells of a confined carstic aquifer in Ingolstadt, Germany, show less than 7 percent atmospheric activity.

In our opinion, the assumptions on which the ^{14}C method in hydrology are based need to be critically re-examined. It is possible that for some aquifers carbonate exchange between solid and liquid phases in the aquifer changes ^{14}C results to a larger degree than generally assumed.

INTRODUCTION

Until a few years ago the use of radioactive isotopes for water dating was restricted mainly to ^{3}H and ^{14}C. To increase the covered time span for dating and to learn more about processes in the aquifer, studies of other isotopes like ^{32}Si, ^{36}Cl, ^{39}Ar, ^{85}Kr, and U-isotopic ratios were introduced. More recently, our interest has been mainly concentrated on the application of ^{39}Ar because this noble gas isotope with its half-life of 269 years (dating range 50 to 1000 years) has a great potential for geophysical applications. ^{39}Ar, other than ^{3}H or ^{14}C, is essentially in steady state in the environmental system. Man-made contributions to the atmospheric activity were, by 1975, less than 5 percent of the 1940 ^{39}Ar level. A disadvantage of ^{39}Ar is the low specific activity of about 0.11 dpm/lt Ar, which necessitates unusual efforts for the extraction of gas samples from large quantities of water. Furthermore, activities can only be measured in a specially shielded low-level counting laboratory. However, these problems can be solved as demonstrated by the 40 ^{39}Ar results measured, up to now, in samples extracted from ice and water (compare for extraction and separation technique, Loosli and Oeschger, 1978, and for counting technique our contribution to these proceedings, Loosli, Heimann, and Oeschger, 1980).

^{39}Ar was first applied to ice dating. Good agreement between ^{39}Ar ages and known ages of the samples (mainly from ^{18}O/^{16}O annual layer measurements in several ice cores, Oeschger and others, 1975; 1977) was demonstrated. However, even the first attempts to date groundwater samples showed unexpectedly large discrepancies between ^{14}C and ^{39}Ar

ages (Oeschger and others, 1974; Loosli and Oeschger, 1978). Based on [85]Kr and O_2 measurements on the same samples contamination by atmospheric air as a cause of the discrepancy can be excluded. To learn more of the discrepancy between the two dating methods, systematic measurements, especially on horizontal profiles in well studied confined aquifers were started. Several other isotopes like ^{18}O, ^{13}C, ^{3}H, partly [32]Si, and noble gas isotopes were measured together with ^{14}C, [39]Ar, and [85]Kr to get as much information as possible.

Most of the data and interpretations in this paper were published earlier (Loosli and Oeschger, 1978). New important results are the [39]Ar determinations for Ingobräu und Buschletten, Ingolstadt/FRG, which show for the first time [39]Ar groundwater activities below the detection limit. The main reason for presenting this paper at this conference, however, is to draw broader attention of the ^{14}C community to this unsolved problem. The need for progress in understanding the meaning of [39]Ar and ^{14}C groundwater ages is especially important in view of waste disposal projects for which reliable information on groundwater is needed.

[39]Ar and ^{14}C results for the aquifer "Greding"

A confined sandstone aquifer in the Frankenalb, Germany, was chosen for [39]Ar and ^{14}C comparison because it was already extensively

Measured [39]Ar-and [14]C- Concentrations in the Aquifer "Greding"
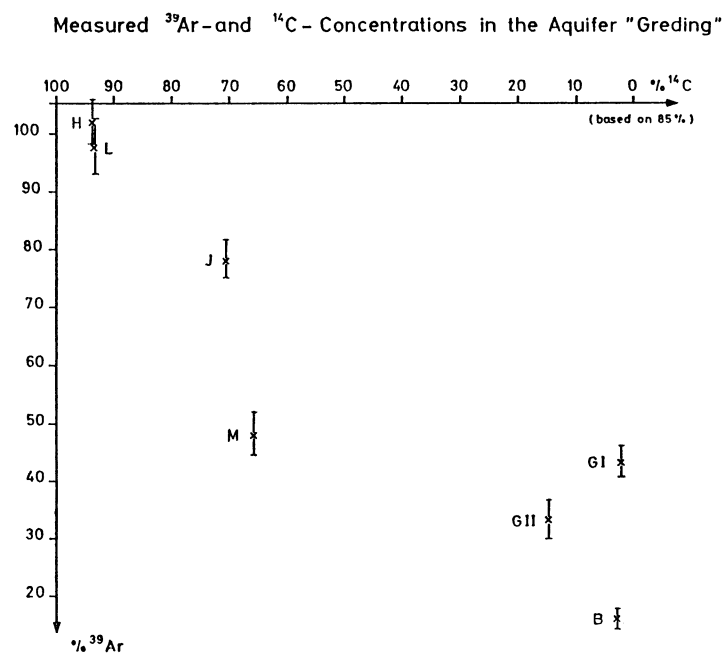

Fig 1. Measured [39]Ar and ^{14}C concentrations in the Greding aquifer. The measured activities show a parallel decreasing trend, but converted to ages, large discrepancies are obvious (T½ [39]Ar: 269 yr; T½ [14]C: 5730 yr). The highest [39]Ar age obtained is about 700 yr, which should be compared with a ^{14}C age of more than 20,000 yr. H: Hilpolt-stein, L: Laibstadt, J: Jahrsdorf, M: Möning, G: Greding, B: Beilngies.

studied (Andres and Geyh, 1970; Geyh, 1972; 1974). Besides ^{39}Ar and ^{14}C, ^{85}Kr, ^{3}H, $\delta^{13}C$, $\delta^{18}O$, noble gas isotope ratios and gas composition were also measured. The ^{39}Ar results are plotted versus the ^{14}C results (corrected for an initial ^{14}C concentration of 85 percent) in figure 1. A decreasing trend of the specific activities of both isotopes in the direction of decreasing hydro-isolines is observed. However, due to the different half-lives strong discrepancies exist between the radioactive ages, as given in figure 2.

The Hilpoltstein and Jahrsdorf wells are located near the recharge area and both contain measurable quantities of ^{3}H and ^{85}Kr. In the other samples, only upper limits of about 2 TU for the ^{3}H activity were measured. With the exception of Laibstadt, the ^{85}Kr activity in the other samples was also low, indicating very limited contamination of the samples. Laibstadt is situated near the recharge area and has a thinner
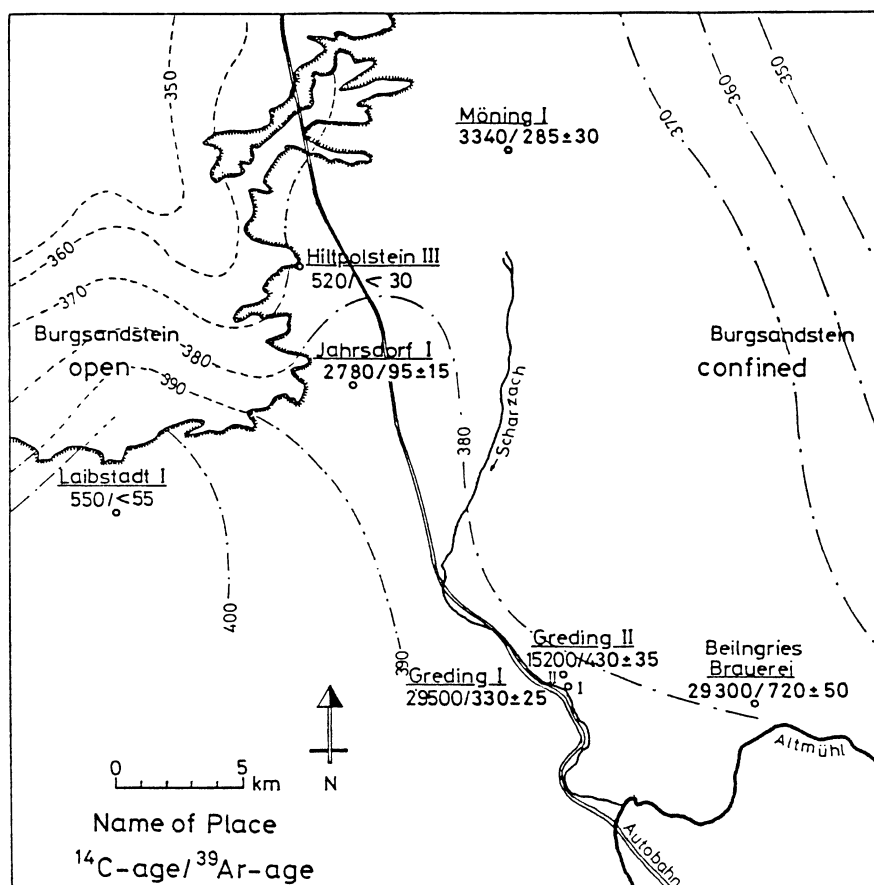

Fig 2. Apparent ages for the Greding aquifer. In the situation map, the apparent ^{14}C and ^{39}Ar ages are plotted together with the hydro-isolines. Large discrepancies of the ages can be seen.

aquiclude than the other wells. For Laibstadt, a contamination of the samples is possible. The [4]He contents measured in the extracted gases by P Bochsler (1978, pers commun) show a clear increase parallel to the decreasing ^{14}C and [39]Ar activities. The $\delta^{18}O$ values decrease from about -9.6‰ near the recharge area to -10.7‰ for the older samples like Greding and Beilngries. Other parameters like pH, free H_2CO_3, water temperature, and $\delta^{13}C$ do not show such systematic behavior with increasing ages, although, especially for pH and $\delta^{13}C$, an increasing respectively decreasing trend can be observed.

Results of other aquifers

Another horizontal profile of 4 samples was collected in Ingolstadt, Germany. This carstic aquifer was previously studied by Apel (1971) (see table 1). Two of the samples showed a [39]Ar activity below the detection limit (Ingobräu, Buschletten). The upper limits given are due to the statistical counting errors. The ^{14}C activity of the 4 samples decreases in the flow direction from 44 to 30 percent modern. The [39]Ar ages for Augraben and Krautbuckel (although preliminary) again significantly deviate from the ^{14}C ages. Similar discrepancies were previously observed for two wells near Nürnberg, Germany (Eckenhaid, Schnaittach) and for two Austrian wells (Grafendorf I and III). For more details, compare Loosli and Oeschger (1978).

The last two samples given in table 1 were extracted from thermal springs. Both are low in [14]C. The [39]Ar value obtained for the thermal spring Zurzach, Switzerland, is the only one thus far to show a [39]Ar activity significantly higher (380 percent) than the atmospheric activity value (100 percent). This demonstrates that aquifers exist with significant underground [39]Ar production. The other thermal spring (Bad Gögging) measured so far, does not show excess [39]Ar activity, but at present, it cannot be decided whether some, or how much, of the observed 41.5 percent modern activity is due to underground produced [39]Ar.

From the ^{3}H values given in table 1 it further can be concluded that fresh water additions can be neglected for all wells considered. Con-

TABLE 1

Results of other samples

	[14]C (% modern)	$\delta^{13}C$ (‰)	[39]Ar (% modern)	[3]H (TU)	$\delta^{18}O$ (‰ SMOW)
Augraben	44 ± 0.4	−11.83	37 ± 14 (prelim)	<1.2	− 9.98
Krautbuckel	41.5 ± 0.4	−11.72	23.3 ± 2.6 "	<1	−10.00
Ingobräu	32.8 ± 0.4	−11.94	< 8.4	<1	− 9.91
Buschletten	30.2 ± 0.4	−11.95	< 7	<1	−10.03
Eckenhaid	55.9 ± 1.3%	−16.66	82.4 ± 6	<2.3	− 9.07
Schnaittach	4.7 ± 3.4%	−11.12	23 ± 4.4	<2.3	−10.74
Grafendorf I	41.1 ± 1	−12.10	31.4 ± 2.4	<0.5	− 8.92
Grafendorf III	44.9 ± 1	−11.13	36.6 ± 3.3	3.9 ± 4.0	−8.90
Zurzach	4.6 ± 0.16	− 9.51	380 ± 10	<0.3	−10.3
Bad Gögging	5.2 ± 0.25	− 6.37	41.5 ± 3.7	<0.6	−10.95

tamination of the samples by atmospheric air during extraction or laboratory processing can furthermore be excluded from the ^{85}Kr and O_2 measurements.

Discussion of possible explanations for the $^{39}Ar/^{14}C$ discrepancy in ages

First, it must be realized that, for mixtures of water of different ages, apparent radioactive ages obtained with radioisotopes of different half-lives do not agree. As an example, let us consider a mixture of 50 percent water with age zero and 50 percent water that is infinitely old. The observed activity, independent of the half-life of the isotope would be 50 percent and the apparent age equal to one half-life. The case of mixing of recent and infinitely old water is shown by the diagonal in a ^{39}Ar versus ^{14}C plot (fig 3). Model calculations suggest exponential age distribution for some groundwater systems. The correspondence between ^{39}Ar and ^{14}C activities for exponential age distributions as a function of the mean age is also shown in figure 3. For piston flow, radioactive ages should agree exactly. In all instances, the measured pairs of ^{39}Ar and ^{14}C activities should lie on the diagonal or to the right of it. This is, eg, the case for the Grafendorf wells, for Möning, Augraben, and Krautbuckel. Other wells such as Greding, Beilngries, Schnaittach, and Bad Gögging have data pairs which are on the left "forbidden" zone of the
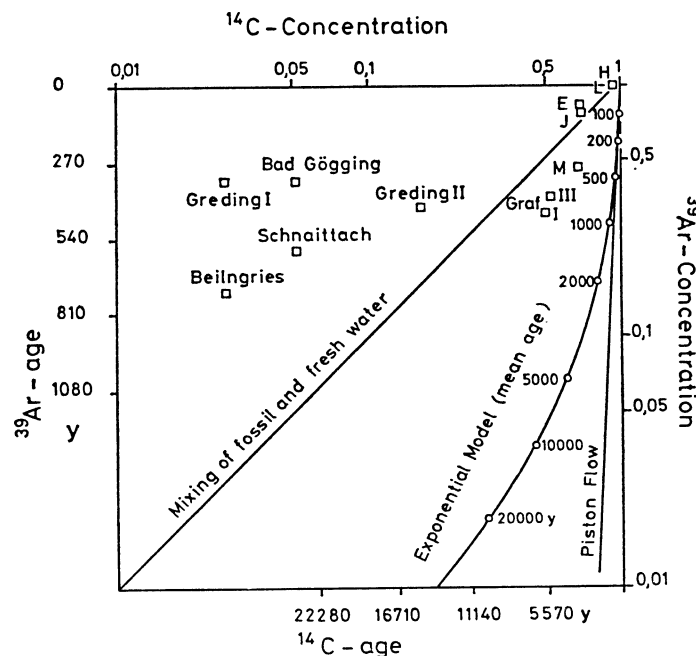

Fig 3. Theoretical relationships between ^{39}Ar and ^{14}C concentrations for three different mixing models. As examples, data is given for the Greding aquifer (corrected for $^{14}C_{ini} = 85\%$), for the Grafendorf well ($^{14}C_{ini}$ used as in Przewlocki, 1975) and for the Schnaittach, Eckenhaid, and Bad Gögging wells.

diagram. The discrepancy in the apparent [39]Ar and ^{14}C ages, therefore, cannot be explained by mixing water with different ages only.

In the following, we discuss some weaknesses of both methods. These include 1) diffusion of air through aquiclude, 2) underground production of [39]Ar, 3) assumptions regarding initial ^{14}C concentrations, 4) dissolution of ^{14}C free carbonates, and 5) chromatographic delay of Σ CO_2 flow relative to water flow.

Diffusion through aquiclude

Too young [39]Ar ages can possibly be explained by gas exchange through the aquiclude which would affect [39]Ar more than ^{14}C since free CO_2 in the water will participate only for CO_2 exchange.

The observed systematic increase of [4]He(originating from decay of the U- and Th-series) in the flow direction of the Greding aquifer, however, leads to the conclusion that diffusion of gases is not fast enough to account for a significant alteration of the [39]Ar activity in the aquifer.

Underground production of [39]Ar

The results given above indicate: 1) For the water from the Zurzach thermal spring a [39]Ar activity 3.8 times modern activity was observed in 3 different samples. This is due to underground production of [39]Ar. The water has been in contact with granitic rocks; its surface temperature is still about 40°C. 2) In the carstic aquifer of Ingolstadt two samples were lacking any detectable [39]Ar activity. Therefore, aquifers exist in which underground production of [39]Ar can be neglected. 3) For the horizontal profile of the Greding aquifer we can assume that the lowest [39]Ar concentrations (about 20 percent modern for Beilngries; similar to that measured in Schnaittach) respresent an equilibrium value for the underground production. The discrepancy between ^{14}C and [39]Ar ages, then, would still exist for samples like Greding I and II and Möning. A further assumption to explain the discrepancy would be necessary, eg, we would have to assume that the underground U-, Th and K-contents decrease for this aquifer for older samples. However, this additional assumption contradicts the measured K-content of the water.

The main reaction to produce [39]Ar in an underground aquifer is the exothermal reaction [39]K(n, p) with neutrons originating mainly from (α, n) processes. The expected specific activity depends on the assumptions of n fluxes and energy spectra, K-content, cross-sections, diffusion of [39]Ar from the rock matrix into the water, pore volume, and Ar content in the water. In addition, the possibility might be considered that a water flow could act as a sink and concentrate underground produced isotopes (like [4]He) from adjacent rock layers. An upper limit for the expected specific [39]Ar activity in a sandstone aquifer was previously estimated at about 4 times the atmospheric level (Loosli and Oeschger, 1978), when neglecting the diffusion of [39]Ar from the upper or lower aquiclude into the water flow. This approximation is an upper limit because it was assumed that the diffusion of [39]Ar from the target matrix into the water is so fast that essentially no [39]Ar decays during the diffusion time. Further,

it was assumed that ^{39}Ar is only diluted with pore waters. This estimate is highly uncertain. Further improvements can be made by measuring samples from thermal water springs originating from different rock types.

Initial ^{14}C concentration

Many careful studies using $\delta^{13}C$ and carbonate chemistry in model calculations lead to the conclusion that the initial ^{14}C concentrations uncertainty in an aquifer can influence the age by, at most, a few thousand years. Therefore, the discrepancy between ^{39}Ar and ^{14}C ages cannot be fully explained by the uncertainty of the initial ^{14}C concentration alone.

Dissolution of ^{14}C free carbonates

Additional dilution of ^{14}C free carbonates, eg, for the Greding aquifer is suggested by systematic trends of water hardness and $\delta^{13}C$ values with the water "age". This can be corrected for by using the ^{14}C to H_2O ratio instead of the $^{14}C/^{12}C$ values. But again, eg, for the ^{14}C ages of the Greding profile, corrections of "only" a few thousand years result, which, by themselves do not explain the discrepancies.

Delay of CO_2 flow relative to the water flow

A chromatographic effect, as observed for many ions in a water flow (important, eg, for long-lived fission products of disposed radioactive waste), or for multiple organic tracers (Cicciolo and others, 1978), could also be a reason for a delay of CO_2 flow relative to the water flow. Such reversible exchange processes were studied by Wendt and others (1967), Münnich (1968), Thilo and Münnich (1970), and Pearson and Hanshaw (1970). $\delta^{13}C$ values would not necessarily help to detect these processes. In laboratory experiments irreversible losses of ^{14}C were also observed (Thilo and Münnich, 1970). It is obvious that more information on underground exchange processes is needed from additional laboratory and field experiments.

In conclusion, we must admit that the $^{14}C/^{39}Ar$ discrepancy is not yet solved. Several causes possibly contribute to the discrepancy and, for both dating methods, more general information is needed. The weak point of the ^{39}Ar method is its underground production. Production rate calculations, more measurements of ^{39}Ar in different type aquifers and a combination with noble gas measurements (especially ^4He, $^{40}Ar/^{36}Ar$, and U-isotopes) are planned.

Additional investigations are also necessary for confirmation of the ^{14}C dating method. Multi-isotope measurements, (eg, ^{14}C, ^3H, ^{85}Kr, ^{39}Ar, ^{32}Si, ^{36}Cl, U-isotopes, $\delta^{13}C$, $\delta^{18}O$, noble gas isotopes) for well-known confined aquifers should be combined with chemical, geologic, and hydrologic studies. Additional laboratory experiments, eg, for exchange processes also seem necessary. Ultimately, comprehensive model studies should lead to a consistent understanding of the complicated processes in an aquifer.

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DISCUSSION

Srdoc: Could you give us a brief description of the experimental procedure and water processing used in [39]Ar measurements?

Loosli: A normal gas sample is extracted from about 15 tons of water, whereas for special samples such as ocean water, at least 1 ton of water has to be outgassed. Normal argon samples of about 2L of argon are measured in a 50cc copper counter with about 40atm pressure. For the especially small samples, 16cc counters with a background of about 0.025cpm are used.