ELSEVIER

Chemical Geology 120 (1995) 127–134

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

^{32}Si in limestone aquifers

U. Morgenstern[a,α], R. Gellermann[a,β], D. Hebert[a], I. Börner[a], W. Stolz[a], R. Vaikmäe[b], R. Rajamäe[b], H. Putnik[b]

[a]*Institute of Applied Physics, TU Mining Academie of Freiberg, Cotta-Straße 4, D-09596 Freiberg, Germany*
[b]*Institute of Geology, Estonian Academy of Sciences, 7 Estonia Avenue, EE-0100 Tallinn, Estonia*

Received 13 January 1993; revision accepted 23 September 1994

Abstract

This paper reports an investigation into the potential application of ^{32}Si as a dating tool for groundwater in limestone aquifers. Refinements to previous techniques are described, which produced a detection limit of 0.1 mBq m^{-3}, compared to a level of ~ 5 mBq m^{-3} in rainwater. Water from wells tapping Estonian limestone aquifers showed significant and decreasing ^{32}Si concentrations down to 50 m. At greater depths, concentrations were below detection limits. This indicates input of cosmogenic ^{32}Si into the aquifer with initial concentration estimated to be 2.5 ± 0.5 mBq m^{-3}, but also shows that ^{32}Si is sorbed during passage through the soil, as well as in the limestone aquifer. Results from karst springs in the Thuringian Basin and Poland, and an aquifer in Saxony-Anhalt, were similar. Comparison with tritium results indicates that non-radioactive (geochemical) processes reduce the measured ^{32}Si concentrations in many cases by more than one order of magnitude below expectation. Consequently, despite a favourable half-life (140 yr) between tritium and ^{14}C, ^{32}Si cannot be applied successfully to date karst waters in the age range between these two isotopes.

The depth profile and ^{32}Si vs. ^{14}C relationship for the Estonian aquifer show some regularities which may, after further investigation of geochemical factors, allow the application of ^{32}Si as an additional age indicator for young groundwater, in cases where tritium data do not provide sufficient information or accuracy.

---

1. Introduction

Following its first detection in nature by Lal et al. (1960), the applicability of ^{32}Si in groundwater dating has been investigated in several studies (Nijampurkar et al., 1966; Lal et al., 1970; Kater and Fröhlich, 1977; Fröhlich et al., 1988). It was at first hoped to obtain a suitable indicator capable of closing the dating gap between tritium (^{3}H, half-life 12.43 yr) and radiocarbon (^{14}C, half-life 5730 yr). But the first studies revealed problems which caused the method to be viewed rather sceptically. The main reasons for this assessment were:

(1) ^{32}Si can obviously be sorbed during recharge through soil and therefore its use as a dating tracer is at least restricted.

(2) The half-life of ^{32}Si has not been known with sufficient accuracy for a long time. Presently its accepted value is 140 ± 20 yr (Kutschera et al., 1980; Alburger et al., 1986; Hofmann et al., 1990).

[MB]

Present addresses:

[α] Geological and Nuclear Sciences, 30 Gracefield Road, PO 31312, Lower Hutt, New Zealand.

[β] Trischler und Partner GmbH, Hafenstraße 60, D-38112 Braunschweig, Germany.

SSDI 0009-2541(94)00115-4

(3) ^{32}Si is an emitter of weak β radiation, found in very low concentration in water (of order of mBq m^{-3}), and consequently the expense of detection is high.

In a study at the Freiberg University of Mining and Technology (Franke et al., 1988), the sorption of ^{32}Si in soil was confirmed directly by ^{32}Si measurements of soils. Additionally, some very young groundwaters were found which contained no measurable ^{32}Si. However, other water revealed concentrations in accordance with expectation. The depth distribution in a sandy aquifer agreed quite well with hydrological models and tritium data. Long-term observations of ^{32}Si in a deep well in a sandy aquifer gave a significant decrease of concentration, which could be correlated with changes in the age distribution indicated by ^{14}C. Furthermore, first measurements of ^{32}Si in groundwater from limestone aquifers yielded results which showed reasonable agreement with tritium data (Fröhlich et al., 1988). Following these results, it was concluded that the next task for investigation should be to determine suitable aquifer types for ^{32}Si groundwater dating.

From the evidence of the available data, limestone aquifers were targetted. Samples were collected in Estonia during 1989. Results for three karst springs in Thuringia, Germany, and one limestone well in Saxony-Anhalt, Germany, sampled during 1985–1987, are also included in this report.

2. Geographic and geologic setting

The Estonian samples were collected from wells near Pärnu in western Estonia and Tallinn in northern Estonia (Fig. 1a). The aquifer type is "Devonian and Silurian marine carbonates". Expectation of water ages at the selected sites, based on previous isotope studies, was in the range recent to >2000 yr, corresponding to the potential range of usefulness of ^{32}Si. Some parameters of the wells appear in Table 1. Sample T*2* may be influenced by river water because the well site is only 50 m from the Pärnu river.

The Thuringian karst springs (details in Table 1) are in the Thuringian Basin in central Germany (Fig. 1b). The aquifer type is "Carbonatic karst of middle Germanic Triassic (Muschelkalk)" (Dietrich, 1975). Earlier isotope studies (Dietrich and Hebert, 1986) showed that these springs discharge water of predominantly young or moderate age. The aquifer type of the well at Steigra, near Querfurt in Saxony-Anhalt, is uncovered "Muschelkalk". It was measured previously by Fröhlich et al. (1988) (their sample *505*). The ^{32}Si concentration was 10.4 ± 1.0 mBq m^{-3}, which appeared unusually high. To check this anomaly, the residual SiO_2 was remilked and measured again (sample QP*51*), and the well was resampled in 1987 (code name QP*52*).

3. Methodology

3.1. Sampling

Detection of the very low levels of ^{32}Si in natural waters requires extraction of silica from several m^3 of water. The extraction can be achieved satisfactorily by coprecipitation with ferric hydroxide. The coprecipitation method became more practicable in the field by using foldable plastic basins and coagulation agents to reduce the settling time (Gellermann et al., 1988). By repeat fillings of 5 plastic basins, each of 0.5-m^3 capacity, 3–4 m^3 of water per day could be processed in the field. Table 2 gives relevant details of the samples and procedures.

Quantitative silica extraction is not necessary for accurate determination of the ^{32}Si concentrations, which can be calculated from the specific activity of ^{32}Si in the extracted silica ($a^{32}{}_{\mathrm{Si}}$) and the concentration of dissolved silica in the sample (C_{silica}):

$$C_{^{32}\mathrm{Si}} = a_{^{32}\mathrm{Si}} C_{\mathrm{silica}} \qquad (1)$$

A field measurement of silica concentration was made to estimate in advance the required sample size, and the residual concentration during coprecipitation was monitored to ensure that the required recovery efficiency was achieved. Silica concentrations were measured precisely in the laboratory (Table 2).

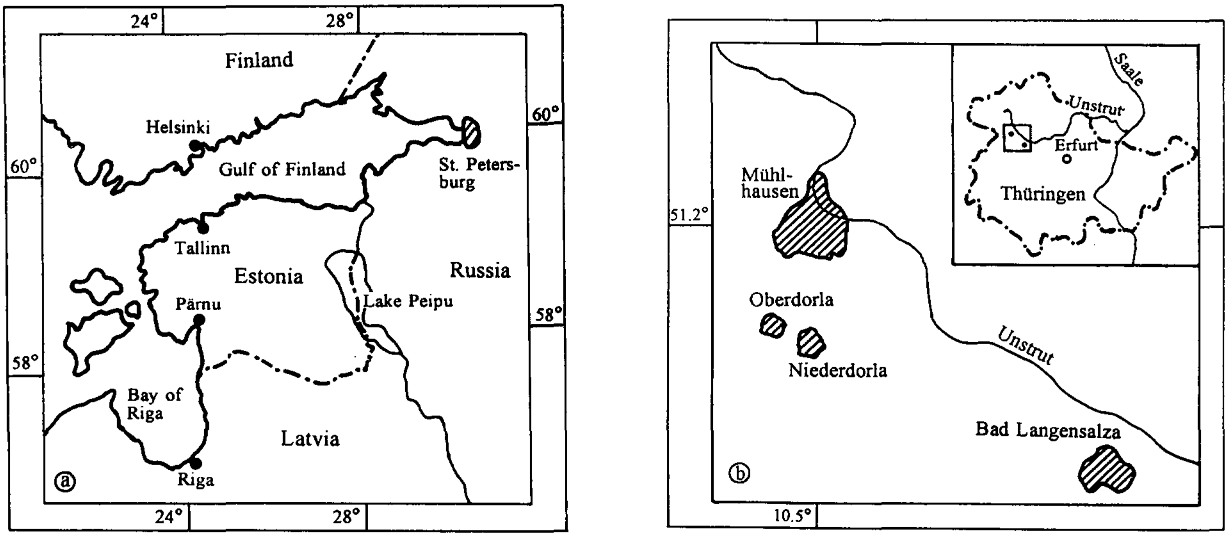

Fig. 1. Location of the studied Estonian (a) and Thuringian (b) aquifers

Table 1
Description of the karst wells and springs

Sampling date	Code No.	Location	Type	Depth (m)
Jun. 26, 1989	T*1*	Tallinn, Koldestreet	well, No. *722* A	59
Jun. 22, 1989	T*2*	Pärnu (fishing plant)	well	29
Jun. 21, 1989	T*3*	Pärnu, Reiu	well	56
Jun. 27, 1989	T*4*	Tallinn, Lake Ülemiste	well	10
Jun. 28, 1989	T*5*	Tallinn, Männiku	well	40
Dec. 2, 1986	*004*	Mühlhausen, historisches Brunnenhaus	spring	–
Dec. 3, 1986	*009*	Bad Langensalza, Großer Golken	spring	–
Dec. 4, 1986	*007*	Oberdorla, Melchiorquelle	spring	–
Jun. 18, 1985	QP*51*	Steigra, well *5*	well	55–71
Jun. 17, 1987	QP*52*	Steigra, well *5*	well	55–71

Additional samples were collected for determination of tritium and ^{14}C.

3.2. Analytical method

^{32}Si concentrations were measured by counting its daughter ^{32}P. Chemical procedures in the laboratory comprise three principal steps. The silica must first be extracted from the precipitate and purified. It is then stored for ~3 months to allow the daughter nuclide to equilibrate (half-life 14.3 days). About 2 weeks before counting, a precise amount of carrier phosphate is added to make the total $Mg_2P_2O_7$ content of the sample 62 mg. In the third step, the phosphate is re-extracted (milking). It contains ^{32}P with an activity corresponding to that of ^{32}Si in the silica. Finally the decaying ^{32}P is measured in a low-level counter for a period of ~40 days. The residual silica can be stored, in case another measurement is needed. Detailed description of the chemical procedures can be found in Gellermann et al. (1988).

Table 2
Data of chemical extraction (sampling, purification and milking)

Code No.	SiO_2 ($mg\,l^{-1}$)	SiO_2 recovered (g)	Equivalent volume (m^3)	$Mg_2P_2O_7$ recovered (mg)	Milking efficiency
T*1*	10.0	37.6	3.76	53.0	0.829
T*2*	9.9	24.9	2.51	58.5	0.925
T*3*	12.0	20.0	1.67	61.1	0.956
T*4*a	4.2	9.8	2.33	60.4	0.949
T*4*b		9.3		58.2	0.910
T*5*	9.6	27.3	2.84	58.4	0.924
004	10.0	21.0	2.10	61.6	0.975
009	10.4	10.4	1.00	59.4	0.934
007	8.0	5.9	0.74	61.6	0.970
QP*51*	11.1	10.2	0.92	52.7	0.830
		9.6		58.3	0.918
QP*52*	10.7	16.9	1.58	63.6	1.000

Table 2 shows that the recovery of carrier phosphate (milking efficiency) varies in the range 80–100%. Independent inductively coupled plasma atomic emission spectrometric (ICP–AES) analysis of the P content in 13 re-extracted $Mg_2P_2O_7$ samples gave a value 27.13±0.14% by weight, close to the theoretical value 27.83%, indicating 97.5% chemical purity of the counted samples, and that the milking efficiency values are correct to better than ±1%.

3.3. ^{32}P beta assay

The counting arrangement used in previous studies (Kater and Fröhlich, 1975; Hebert et al., 1986) was restored in 1991. Radiochemically pure $Mg_2P_2O_7$ prepared from the samples is sandwiched between two PIPS detectors (Canberra®, model B-*300*-AM, active area 300 mm^2). Because of radon problems in the underground laboratory at Bergakademie Freiberg, this 4π detector arrangement was moved to the surface laboratory, where an anticoincidence shielding system (Geiger–Müller tubes) and passive shielding by iron, paraffin with boron, mercury, lead and electrolyte copper were used. Recent system parameters are compiled in Table 3.

Table 3
Characteristic parameters of the ^{32}Si measurement device

Background count rate	B	(cph)	3.35
Blank sample count rate		(cph)	4.97
Counting efficiency	η_D		0.657
Figure of merit	$\eta_D/B^{1/2}$	($hr^{1/2}$)	0.295
Detection limit (2σ)		($mBq\,m^{-3}$)	0.1

The background was measured without $Mg_2P_2O_7$ and the blank sample was $Mg_2P_2O_7$ milked without SiO_2

4. Results

Fig. 2 shows gross beta activity as a function of $e^{-\lambda t}$ (λ=disintegration constant for $^{32}P=0.0485$ day^{-1}, t=time from milking) for the Estonian samples.

Sample T*4* was milked and counted twice, and the result indicates satisfactory reproducibility of the radiochemical procedure. The result of sample T*3* is identical to the blank measurements and confirms the radiochemical purity of all chemicals and processes.

Net ^{32}P count rates and ^{32}Si data are given in Table 4. Additionally, the results for tritium (^3H), ^{14}C and $\delta^{13}C$ are given. The ^3H data are used to estimate mean residence times (T_M), using the exponential age distribution. For the Es-

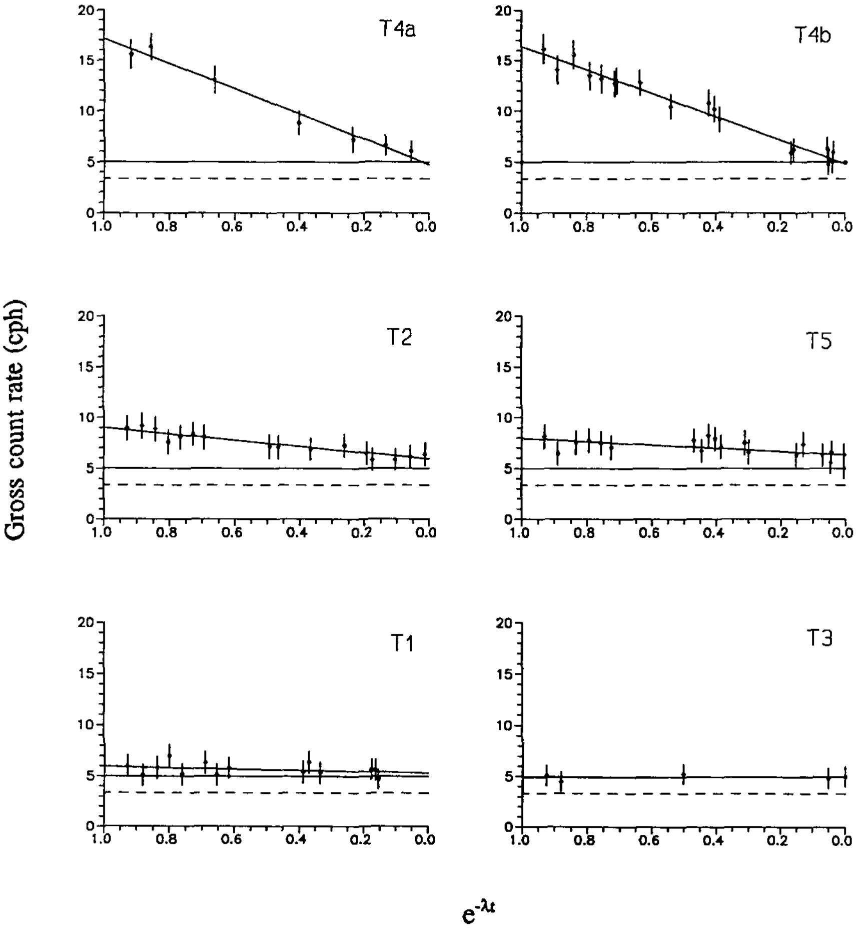

Fig. 2. Plots of daily gross beta activity vs. $e^{-\lambda t}$ for all Estonian samples. The *full lines* indicate the mean blank count rate and the *dotted lines* indicate the mean background count rate. Errors indicated are 1σ counting statistics.

tonian samples, these are only approximate estimates, because they were calculated from single ^{3}H results using the Freiberg tritium input function.

^{32}Si data for some young karst waters from the Thuringian basin are also included in the second part of Table 4. In this case, tritium data sets over the period 1980–1986 were available to apply in estimating the mean residence times.

The unexpectedly high result reported by Fröhlich et al. (1988) (code No. *505*) was checked by remilking the SiO_2 twice (QP*51*), and a new sample (QP*52*) was collected. All these checks yielded lower concentrations (Table 4). Ignoring the high result, the maximum ^{32}Si concentration in groundwaters measured at the Freiberg laboratory is ~ 5 mBq m^{-3}, the same as the mean value in precipitation (Franke et al., 1986).

5. Discussion

The ^{32}Si data of the 5 Estonian wells (Table 4) decrease down to 50-m depth (Fig. 3). At greater

Table 4
Isotope data of groundwaters from limestone aquifers in Estonia (1989) and Saxony-Anhalt (1985, 1987) and of karst spring waters from the Thuringian Basin (1986)

Depth (m)	Code No.	Net ^{32}P count rate (cph)	^{32}Si (mBq m^{-3})	^{3}H (TU)	^{14}C (pmC)	$\delta^{13}C$ (‰ vs. PDB)	T_M (yr)
10	T*4*	12.4±0.5 11.6±0.4	2.4±0.3 2.4±0.3	30±2	103.7±0.4	–	20±10
29	T*2*	3.0±0.4	0.6±0.1	33±1[a]	88.5±0.3	−13.8	20±10
40	T*5*	1.6±0.5	0.3±0.1	38±2	59.1±0.7	–	20±10
56	T*3*	−0.1±0.3	<0.1	13±1	49.8±0.3	−8.8	120±20
59	T*1*	0.6±0.5	0.1±0.1	<0.5	19.8±0.3	−15.5	>2,000
–	*004*	1.4±0.3	0.3±0.1	36±2	71.4±0.7	−12.8	36±4
–	*009*	1.5±0.3	0.7±0.1	34±2	63.3±0.7	−12.5	30±0
–	*007*	1.4±0.4	0.8±0.3	39±2	83.3±0.8	−13.6	11±3
55–71	QP*51*	0.4±0.2 0.4±0.2	0.2±0.1 0.2±0.1	27±3	82.0±0.5	−15.0	40±10
55–71	QP*52*	0.5±0.5	0.1±0.1	37±2	84.3±0.9	−14.7	30±10

T_M represents the mean residence time of the water estimated by fitting the exponential model curves to the tritium data. Errors indicated for activity concentrations are 1 standard measurement error; routine standard error for $\delta^{13}C$ is ±0.1‰.
[a] Pärmu river 29±2 TU.

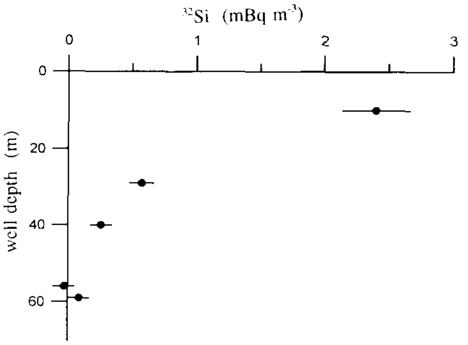

Fig. 3. Plot of ^{32}Si activity vs. well depth.

depth the concentrations are below the limit of detection.

The samples with detectable concentrations all had tritium concentrations of > 30 TU, indicating mean residence times of ~ 20 yr.

In the ^{32}Si–^{14}C diagram (Fig. 4), all Estonian and most other limestone values show a consistent pattern.

For the exponential model, the steady state solution for the output tracer concentration is:

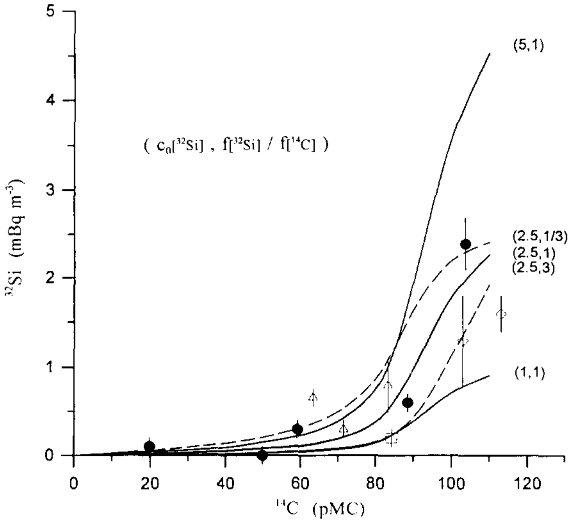

Fig. 4. Plot of ^{32}Si vs. ^{14}C. The theoretical curves indicated correspond to the ^{32}Si input concentration $c_0[^{32}Si]$ and the ratio of geochemical factor f of ^{32}Si and ^{14}C. ^{14}C-values are not corrected for $\delta^{13}C$. For sample code see Fig. 5.

$$C=\frac{c_0}{1+(f\lambda)T_M} \quad (2)$$

where c_0 is the input concentration and f represents a geochemical factor which quantifies the removal of tracer by processes other than radioactive decay. Eliminating T_M allows relationships between ^{32}Si and ^{14}C to be predicted. In Fig. 4, the ^{14}C calculation assumed $c_0[^{14}\mathrm{C}] = 90$ pmC for the pre-bomb situation and took account of the likely rise for post-bomb waters. The assumed half-life of ^{32}Si was 140 yr. The theoretical curves in Fig. 4 represent various ^{32}Si input concentrations and ratios of the two geochemical factors f. A reasonably good fit of the data to the theoretical curves is obtained in the case of $c_0[^{32}\mathrm{Si}] = 2.5 \pm 0.5$ mBq m^{-3}. This value appears to be the ^{32}Si input concentration.

To obtain age information independent of retardation, the mean residence times T_M were estimated from tritium data, again by using the exponential model. These residence times (Table 4) and the ^{32}Si concentrations are plotted in Fig. 5, which also shows theoretical curves caused by radioactive and non-radioactive losses representing various ^{32}Si input concentrations and geochemical factors f. For completeness, the other limestone aquifer samples from Fröhlich et al. (1988) are included.

Although incomplete geohydraulic information allows only rough estimation of T_M, it is apparent that in many cases the ^{32}Si contents are by more than an order of magnitude too low. The result for the young karst waters from the Thuringian Basin are similar (Table 4; Fig. 5). It is obvious that the ^{32}Si in groundwaters from limestone aquifers is retarded over the whole range measured earlier for other aquifer types (Fröhlich et al., 1988).

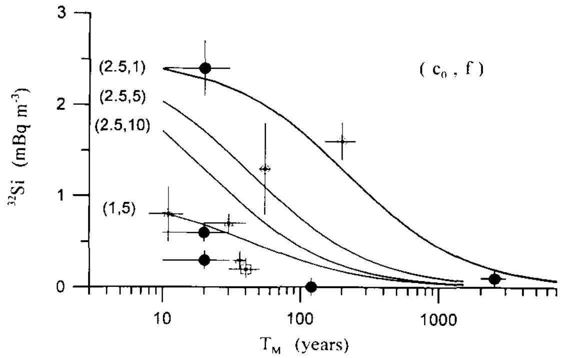

Fig. 5. ^{32}Si vs. mean residence time of groundwater T_M estimated from tritium data. The theoretical curves indicated are (c_0,f). The aquifers are limestone from Tallinn and Pärnu in Estonia (●), Mühlhausen in Thuringia (△), Steigra in Saxony-Anhalt (□) and Katowice in Poland (◇).

6. Conclusions

(1) The ^{32}Si result of the depth profile of the Estonian well waters shows that the measurement procedures were sufficiently sensitive and reproducible to record the ^{32}Si concentrations of groundwaters.

(2) Furthermore, this result proves that cosmogenic ^{32}Si penetrates to the limestone aquifer. The ^{32}Si input concentration to the limestone is estimated to be 2.5 ± 0.5 mBq m^{-3}.

(3) ^{32}Si is strongly sorbed during infiltration of rainwater through the soil overlying the limestone, and within the limestone itself. The geochemical retardation factor covers the range found earlier for other aquifer types. Despite its favourable half-life between T and ^{14}C, ^{32}Si cannot yield meaningful ages, because other processes dominate over the radioactive losses.

(4) The depth profile and the ^{32}Si–^{14}C plot of the Tallinn samples indicate some regularities in the input and the spatial and temporal distribution of ^{32}Si in the shallow zone. Hence ^{32}Si may serve as an additional indicator for the classification of very young groundwaters. Due to its relatively constant input, ^{32}Si may yield additional information in cases where the tritium method yields inconclusive results. But a much better understanding of the factors influencing the geochemical behaviour of ^{32}Si is necessary for the further improvement of this method. The results of this investigation suggest that young groundwaters with high ^{14}C concentration should be selected for such further studies.

Acknowledgements

We thank T. Franke, who conducted the sampling in 1986 in the Thuringian Basin. We are also grateful to H. Gäggeler and R. Keil from Paul Scherrer Institute in Villigen (Switzerland) for the P content determination. For constructing the electronic device we wish to thank S. Henschel. Finally, we thank C.B. Taylor (Geological and Nuclear Sciences, Lower Hutt, New Zealand) for critical discussion and thorough examination of the paper.

References

Alburger, D.E., Harbottle, G. and Norton, E.F., 1986. Half-live of ^{32}Si. Earth Planet. Sci. Lett., 78: 168–176.

Dietrich, P.G., 1975. Zur Hydrogeologie des Mittleren Muschelkalks im Thüringer Becken. Z. Angew. Geol., 21 (8): 384–392.

Dietrich, P.G. and Hebert, D., 1986. Methodische Aspekte isotopenhydrogeologischer und hydrochemischer Untersuchungen an einem Karstgrundwasserleiter der DDR. Freiberger Forschungsh., C417: 76–92.

Franke, T., Fröhlich, K., Gellermann, R. and Hebert, D., 1986. ^{32}Si im Niederschlag von Freiberg — Beitrag zur Untersuchung der Anwendbarkeit von ^{32}Si für die Grundwasserdatierung. Isotopenpraxis, 22: 121–123.

Franke, T., Fröhlich, K., Gellermann, R. and Voland, B., 1988. ^{32}Si measurements in soil samples and implications to the geochemistry of silicon in soil. Isotopenpraxis, 24: 59–62.

Fröhlich, K., Franke, T., Gellermann, R., Hebert, D. and Jordan, H., 1988. Studies of ^{32}Si in different aquifers and implications for groundwater dating. Isotopenpraxis, 24: 355–363.

Gellermann, R., Börner, I., Franke, T. and Fröhlich, K., 1988. Preparation of water samples for ^{32}Si determinations. Isotopenpraxis, 24: 114–117.

Hebert, D., Fröhlich, K., Franke, T., Gellermann, R., Unterricker, S. and Kim, J.H., 1986. Underground laboratory in Freiberg. Nucl. Instrum. Methods, pp. 427–430.

Hofmann, H.J., Bonani, G., Suter, M., Wölfli, W., Zimmermann, D. and Gunten, H.R., 1990. Nucl. Instr. Methods, 52: 544.

Kater, R. and Fröhlich, K., 1975. Meßplatz zur Bestimmung natürlicher ^{32}Si-Aktivitäten. Isotopenpraxis, 11: 103–105.

Kater, R. and Fröhlich, K., 1977. Z. Angew. Geol., 23: 135.

Kutschera, M., Henning, W., Paul, M., Smither, R.K., Stephenson, E.J., Yentna, Y.L., Alburger, D.E. and Harbottle, G., 1980. Measurement of the half-life of ^{32}Si via accelerator mass spectrometry. Phys. Rev. Lett., 45: 592.

Lal, D., Goldberg, E.D. and Koide, M., 1960. Cosmic-ray-produced silicon-32 in nature. Science, 131: 332–337.

Lal, D., Nijampurkar, V.N. and Rama, S., 1970. Silicon-32 hydrology. In: Isotope Hydrology. IAEA (Int. At. Energy Agency), Vienna.

Nijampurkar, V.N., Amin, B.S., Kharkar, D.P. and Lal, D., 1966. Dating groundwaters of ages younger than 1000–1500 years using silicon-32. Nature (London), 210: 478.