# $^{32}Si$ Measurements in Soil Samples and Implications to the Geochemistry of Silicon in Soil*)

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*A procedure for the preparation of soil samples for $^{32}Si$ measurements is described. Two different soil profiles have been studied. The obtained $^{32}Si$ concentrations in these profiles indicate a sorption of $^{32}Si$ on clay, ferric-manganese hydroxides as well as humic matter. On the base of a box model migration velocities of $^{32}Si$ in the soil have been estimated to be about 0·1 to 10 cm · $a^{-1}$.*

*Es wird eine Methode zur Aufbereitung von Bodenproben für $^{32}Si$-Messungen beschrieben. Zwei unterschiedliche Bodenprofile wurden untersucht. Die gemessenen $^{32}Si$-Konzentrationen in diesen Bodenprofilen deuten darauf hin, daß eine Sorption des $^{32}Si$ an Ton, Eisen-Mangan-Hydroxiden, aber auch an humoser Substanz stattfindet. Auf der Grundlage eines Box-Modells wurde die Migrationsgeschwindigkeit des $^{32}Si$ im Boden bestimmt, die ungefähr 0,1 ... 10 cm · $a^{-1}$ beträgt.*

## Keywords

adsorption; age estimation; geochemistry; isotope dating; sample preparation; silicates; silicon 32; soils;

## 1. Introduction

The cosmogenic isotope $^{32}Si$ has been taken into consideration for groundwater dating purposes since more than 20 years [1, 2]. But up to the present several questions have been remained unsolved regarding its behaviour in the hydrosphere. For groundwater studies especially the initial concentration is an important factor. This initial concentration can be determined from the $^{32}Si$ deposition rate on the soil surface, the infiltration rate of water and last but not least it may be influenced by geochemical effects within the unsaturated zone.

Therefore, we made a first attempt to measure $^{32}Si$ in the unsaturated zone. In this paper we describe the chemical procedure used and first results obtained. A more detailed description of the radiochemical purification of silica and milking of the $^{32}Si$ daughter $^{32}P$ are given in [3]. Counting of $^{32}P$ and some systematic tests of the $^{32}Si$ measurements are published in [4].

$^{32}Si$ in soil — basic estimations:

The mean annual $^{32}Si$ deposition in Central Europe amounts to about 4 mBq · $m^{-2}$ · $a^{-1}$ [5]. Based on this value and a half-life of 105 a the total $^{32}Si$ inventory of a thick soil column can be estimated to be 600 mBq · $m^{-2}$.

If a significant part of the $^{32}Si$ migrates through a 5 m thick unsaturated zone and reaches the groundwater table the mean $^{32}Si$ concentration in the soil should be smaller than 120 mBq · $m_{soil}^{-3}$ or 0·06 mBq · $kg_{soil}^{-1}$.

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The detection limit of $^{32}Si$ measurements is in the order of 1 mBq total activity [4]. Consequently, masses of about 20 kg soil are necessary for obtaining a sufficient activity. If sorption processes occur in well defined layers somewhat smaller masses may be sufficient.

However, a radiochemical purification of some kilograms of silica requires high expense and milking some milligrams of $Mg_2P_2O_7$ containing the radioactive $^{32}P$ from some kilograms of silica is practically impossible. $^{32}Si$ measurements of soil samples are only feasible if the studied nuclides are assumed to be located at the grain surfaces and, consequently, can be extracted by incomplete leaching of the soil.

## 2. Experimental

### 2.1. Sampling

Two soil profiles have been studied. The first one was dug in a Pleistocene sand, the second one was taken from a braunerde on gneiss. Both profiles are briefly characterized in Fig. 1.

### 2.2. Leaching

In the laboratory the samples were weighed and roughly crushed. Then they were dried at 120 °C and annealed at 800 °C for 1 h. The remaining masses were determined. The samples were leached with a 2% NaOH solution in a plastic vat for 2 to 3 days. The parameters of this leaching procedure are listed in Tab. 1.

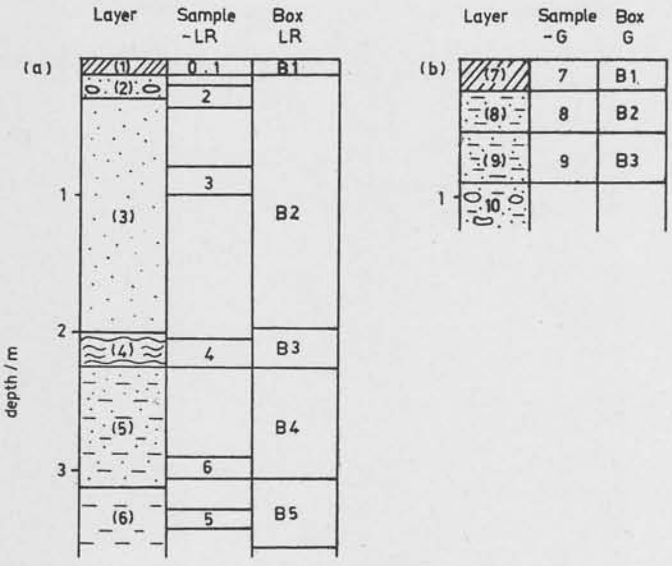


Fig. 1. Characteristics of the sampled soil profiles

Profile L-R:

(1) A-horizon: grey-coloured sand with roots and organic debris
(2) $B_{SV}$-horizon: yellow bleached sand and gravel
(3) $E_g$-horizon: yellow-white bleached silty sand with isolated ferric hydroxide tapes
(4) $B_S$-horizon: wet silty loam brown-coloured by ferric-manganese hydroxides
(5) $B_S$-horizon: like (4) but less hydroxides
(6) C-horizon: Red brown grey-coloured silty clay

Profile G:

(7) A-horizon: Brown coloured soil with roots and organic debris
(8) B-horizon: Light brown-coloured loam
(9) $C_1$-horizon: Light grey loam with isolated ferric hydroxides
(10) $C_2$-horizon: Grey-brown loam with weathered gneiss.

After finishing the leaching the samples were centrifuged and washed with deionized water. The remaining soil was discarded and the dissolved silica was precipitated:

(1) By direct precipitation of silica from the alcaline solution with conc. hydrochloric acid.

(2) By coprecipitation of silica with ferric hydroxide.

The former method is faster and easier than the latter and requires less chemicals but it acts not often quantitatively and requires a second precipitation.

The precipitate is treated in an analogue manner as described for water samples [3]. A flow diagram of the whole procedure is given in Fig. 2.

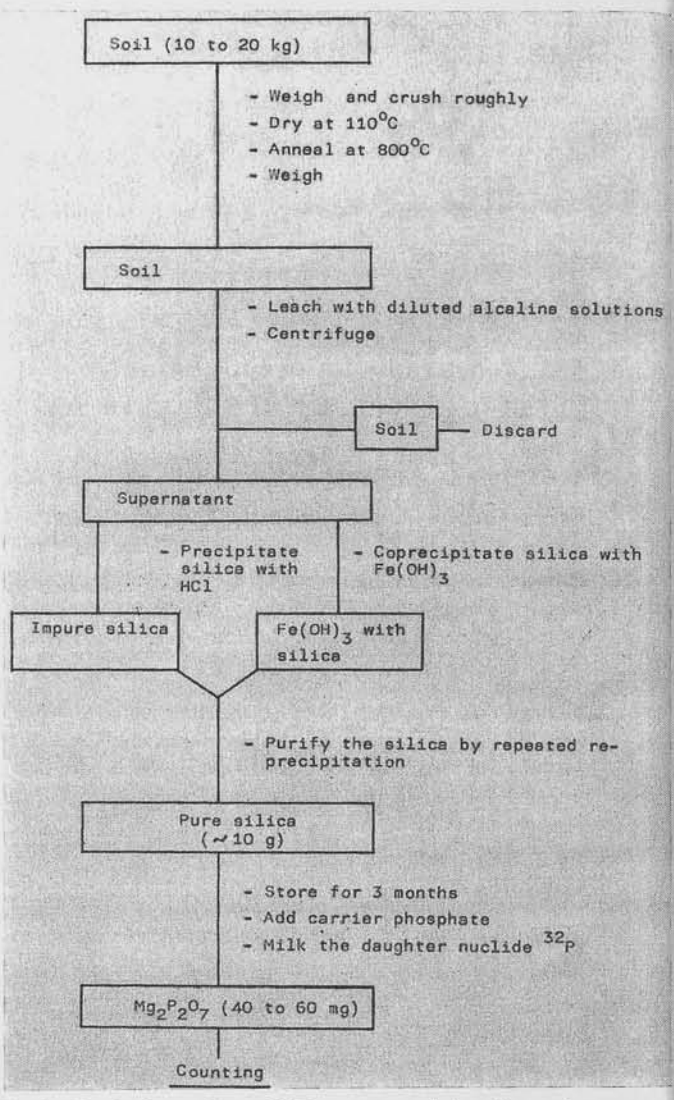


Fig. 2. Chemical procedure of $^{32}$Si measurements in soil samples

## 3. Evaluation of data

The primary result of the $^{32}$Si measurement is the specific activity per gram of silica $a_{SiO_2}$. The interpretation of the results is based on the $^{32}$Si concentration in the soil $C_{soil}$ which is calculated by

$$C_{soil} = a_{SiO_2} \cdot m_{SiO_2} \cdot (1 - p)\, \varrho_{soil}/m_{soil}\,, \qquad (1)$$

Tab. 1. Radiochemical treatment of the soil samples
$m_S$: mass of dried soil; $m_{SiO_2}$: mass of purified silica
(1) direct precipitation with HCl; (2) coprecipitation with ferric hydroxide

| sample | $m_S$ [kg] | leaching agent | leaching Volume [l] | time [h] | $m_{SiO_2}$ [g] | Remarks |
|---|---|---|---|---|---|---|
| S 0/1-LR | 26·80 | NaOH (1%) | 20 | 48 | 7·78 | (1) |
| S 0/2-LR | 26·80 | KOH (50%) | 20 | 96 | 28·45 | (1) |
| S 1-LR | 20·00 | NaOH (2%) | 10 | 47 | 8·00 | (1), (2) |
| S 2-LR | 14·95 | NaOH (2%) | 10 | 53 | 1·65 | (2) |
| S 3-LR | 21·48 | NaOH (2%) | 10 | 60 | 4·70 | (2) |
| S 4-LR | 16·25 | NaOH (2%) | 10 | 60 | 3·80 | (2) |
| S 5-LR | 21·20 | NaOH (2%) | 10 | 60 | 19·90 | (2) |
| S 6-LR | 10·10 | NaOH (2%) | 10 | 60 | 6·80 | (2) |
| S 7-G | 10·00 | NaOH (2%) | 10 | 71 | 1·50 | (1) |
| S 8-G | 10·00 | NaOH (2%) | 10 | 74 | 2·15 | (1) |
| S 9-G | 10·00 | NaOH (2%) | 10 | 74 | 8·00 | (2) |

where $\varrho_{soil}$ and $p$ denote the density and the porosity, respectively, of the soil ($\varrho_{soil} = 2{\cdot}65 \cdot 10^3$ kg $\cdot$ m$^{-3}$, $p \approx 0{\cdot}3$). $m_{SiO_2}$ represents the mass of the extracted silica and $m_{soil}$ is the mass of the leached soil.

## 4. Results and discussion

The measured $^{32}$Si activities of the two studied soil profiles are given in Tab. 2.

Qualitatively, these results indicate a sorption of $^{32}$Si by the ferric-manganese hydroxide layer, by the clay and by humic matter. These are important facts for an assessment of the favourable conditions for $^{32}$Si groundwater dating. For instance, aquifers which are covered by thick loam layers should consequently be unsuitable for $^{32}$Si studies. On the other hand, the $^{32}$Si method should be applicable to sandy phreatic aquifers.

Furthermore, the $^{32}$Si measurements permit a quantitative estimation of the silica migration through soil layers by using a simple box model (Fig. 3).

Assuming steady-state conditions the $^{32}$Si transfer from box $i - 1$ to box $i$ can be described by

$$(k_i + \lambda)\, C_i H_i = k_{i-1} C_{i-1} H_{i-1}\,, \qquad (2)$$

where $k_i$ is the transfer coefficient and $H_i$ is the thickness of the layer covered by box $i$. $k_i^{-1}$ can be interpreted as mean residence time of $^{32}$Si in the corresponding box. In order to eliminate the box sizes which are included in the

Tab. 2. Results of $^{32}$Si measurements in two soil profiles

| Sample | Depth [m] | $a_{Si\text{-}32}$ [mBq $\cdot$ g$_{SiO_2}^{-1}$] | $C_{Si\text{-}32}$ [Bq $\cdot$ m$_{soil}^{-3}$] |
|---|---|---|---|
| S 0/1-LR | 0 – 0·10 | 0·68 ± 0·05 | 0·37 ± 0·03 |
| S 0/2-LR | 0 – 0·10 | 0·06 ± 0·04 | 0·10 ± 0·09[1] |
| S 1-LR | 0 – 0·15 | 0·22 ± 0·03 | 0·16 ± 0·04 |
| S 2-LR | 0·2 – 0·35 | < 0·1 | < 0·02 |
| S 3-LR | 0·8 – 1·0 | < 0·1 | < 0·04 |
| S 4-LR | 2·1 – 2·3 | 0·6 ± 0·03 | 0·28 ± 0·02 |
| S 6-LR | 2·9 – 3·05 | 0·05 ± 0·03 | 0·06 ± 0·04 |
| S 5-LR | 3·3 – 3·4 | 0·22 ± 0·04 | 0·39 ± 0·08 |
| S 7-G | 0 – 0·2 | 2·60 ± 0·30 | 0·72 ± 0·08 |
| S 8-G | 0·2 – 0·55 | 0·32 ± 0·04 | 0·13 ± 0·02 |
| S 9-G | 0·55 – 0·9 | < 0·04 | < 0·06 |

[1]) Repeated leaching of S 0/1-LR

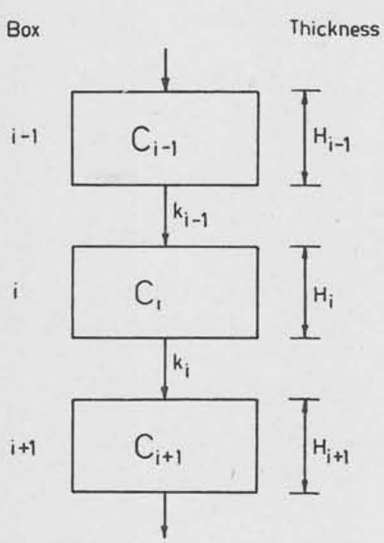


Fig. 3. Box model for the estimation of silica transport in soil

Tab. 3. Estimated $^{32}$Si migration parameters in soil profiles on the base of a box model

For profile G the values have been calculated with deposition rates of 4 mBq $\cdot$ m$^{-2}$ $\cdot$ a$^{-1}$/1·3 mBq $\cdot$ m$^{-2}$ $\cdot$ a$^{-1}$

| Box | $H_i$ [m] | $C_{Si\text{-}32}$ [Bq $\cdot$ m$_{soil}^{-3}$] | $k_i^{-1}$ [a] | $v_i$ [cm $\cdot$ a$^{-1}$] |
|---|---|---|---|---|
| LR B 1 | 0·10 | 0·25 | 7 | 1 |
| LR B 2 | 1·85 | <0·03 | <16 | >12 |
| LR B 3 | 0·25 | 0·28 | 48 | 1 |
| LR B 4 | 0·85 | 0·06 | 16 | 4 |
| LR B 5 | 0·50 | 0·39 | 184 | 0·3 |
| G B 1 | 0·20 | 0·72 | 47/390 | 0·4/0·05 |
| G B 2 | 0·35 | 0·13 | 16/682 | 2/0·05 |
| G B 3 | 0·35 | <0·06 | <8/(∞) | >4/– |

$k_i$-values mean migration velocities $\bar{v}_i$ can be calculated by

$$\bar{v}_i = k_i H_i\,. \qquad (3)$$

This model was applied to the interpretation of $^{32}$Si measuring results. As $^{32}$Si input rate to the first box the deposition rate of 4 mBq $\cdot$ m$^{-2}$ $\cdot$ a$^{-1}$ was used. The results obtained are summarized in Tab. 3. They characterize quantitatively the layers with a significant $^{32}$Si sorption (especially clay and ferric hydroxides). In the case of soil profile G the increase of the migration velocities with depth can hardly be explained by the geochemical characteristics of the soil (see Fig. 1b). However, the profile G was dug on a slightly inclined slope where a significant part of the precipitation flows off. If we assume that the measured $^{32}$Si represents the total $^{32}$Si inventory in this soil an effective deposition of 1·3 mBq $\cdot$ m$^{-2}$ $\cdot$ a$^{-1}$ results. Using this value uniform and lower migration velocities are obtained. Because the soil of profile G is rich in clay minerals these velocities given in Tab. 3 as the second ones seem to be more reasonable than the first ones. Summarizing the results of this study the following conclusions can be drawn:

(1) $^{32}$Si forms a new and suitable isotopic indicator for studying the silica migration in soil.
(2) First estimations of migration velocities of $^{32}$Si in soil profiles yielded values in the order of 0·1 to 10 cm $\cdot$ a$^{-1}$.
(3) Apart from the bleached sands the migration velocities are significantly lower than the infiltration velocities of water. That means $^{32}$Si moves through most of the studied layers with retardation factors in the order of magnitude 10.
(4) This work has to be interpreted as a first step regarding the use of $^{32}$Si for geochemical studies in soil. The applicability of the methods described in this paper has to be proved by further systematic investigations.

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