

^{210}Pb , ^{226}Ra and ^{32}Si in Pavin lake (Massif Central, France)

J.-M. Martin^a, M. Meybeck^{a,1}, V.N. Nijampurkar^b and B.L.K. Somayajulu^b

^a*Institut de Biogéochimie Marine, Unité Associée au CNRS No. 386, 1 rue Maurice Arnoux, F-92120 Montrouge, France*

^b*Physical Research Laboratory, Ahmedabad 380 009, India*

(Received May 21, 1991; revised and accepted October 11, 1991)

ABSTRACT

Martin, J.-M., Meybeck, M., Nijampurkar, V.N. and Somayajulu, B.L.K., 1992. ^{210}Pb , ^{226}Ra and ^{32}Si in Pavin lake (Massif Central, France). *Chem. Geol. (Isot. Geosci. Sect.)*, 94: 173–181.

Measurements of cosmogenic ^{32}Si and the U-decay series' nuclides ^{210}Pb and ^{226}Ra in waters and sediments of lake Pavin are reported. Both ^{210}Pb and ^{226}Ra are enriched in the anoxic deep waters compared to the oxic surface waters, respectively by a factor of 4 and 10, whereas ^{32}Si is depleted by a factor of ~ 2 . Redox conditions in the lake appear to have no marked effect on the ^{32}Si . Using a steady-state box model it is shown that the deep-water ^{32}Si concentration is controlled by the underground lacustrine springs. The residence times of ^{210}Pb , ^{32}Si and ^{226}Ra are ~ 1 , ~ 10 and ~ 80 a, respectively. In the case of ^{32}Si , where more data are available, the assessed inventory data from the overhead atmospheric fallout and that measured in the sediments agree very well as expected. The ^{210}Pb - and ^{32}Si -based deposition rates during the past ~ 100 a ranged from 0.8 to 1.9 mm a^{-1} , earlier these were a factor of ~ 3 – 5 faster. The geochemistry of ^{32}Si and ^{210}Pb in lake Pavin in many ways resembles that in the ocean, only the time scales of the processes involved are faster.

1. Introduction

In view of the vastness of the oceans and the complexity of marine processes an alternative approach to understand the aqueous biogeochemical processes would be through study of small and well-defined ecosystems. Indeed Volchok et al. (1970) did take such an approach: they studied a crater lake to understand oceanic fallout. A number of earlier works too realised the value of studying geochemical processes in lakes, well defined with respect to their sources and sinks (Lerman, 1978). It is well known that lake sediments are ideal for storing records of short-lived phenomena (Krishnaswami and Lal, 1978).

Due to its geochemical and morphological characteristics, Pavin lake in the Massif Central, France, appears to be ideally suited for such studies (Martin, 1985). It is located in a remote area far from industrial sources. Due to its forested watershed, the lake sediments are basically biogenic, consisting of $\sim 90\%$ diatomous substance with negligible detrital materials. From a chemical point of view the lake is characterised by the presence of two stratified layers, the upper oxic layer (mixolimnion) which is affected only during winter by mixing and the deeper and totally anoxic layer (monimolimnion) which has steady-state conditions (Meybeck et al., 1975). The present investigation, using the U-decay series' nuclide ^{210}Pb (half-life = 22.3 a) and cosmogenic ^{32}Si (= 140 a; see Somayajulu et al., 1987, 1991), is intended to determine the accumulation rates of the lake sediments as well as to understand the aqueous geochemistry of Pb and Si

¹*On leave at: Laboratoire de Géologie Appliquée, Université Pierre et Marie Curie, 4 place Jussieu, F-75230 Paris Cedex 05, France.*

through their radioactive isotopes (Krishnaswami et al., 1971; Koide et al., 1973; Robbins, 1978; Schell, 1982; Lal and Somayajulu, 1984).

2. Materials and methods

Pavin lake (lat. 45° 55' N, long. 02° 54' E) is at an altitude of 1197 m A.M.S.L. (above mean sea level). It is approximately circular (mean diameter = 750 m) in shape with a maximum water depth of ~92 m.

2.1. Sampling

For ^{210}Pb and ^{226}Ra studies, sampling was done during two periods. In September 1975, 50-l water samples were collected and processed for ^{210}Pb and ^{226}Ra after filtration through no. 113 (pore diameter = 5 μm) and/or 0.45- μm Millipore[®] filters. The suspended matter on the filters was analysed for ^{210}Pb . During 1978, large-volume (200 l) samples from both surface and deep waters were collected using PVC (polyvinyl chloride) Niskin[®] bottles. The deep waters smelling heavily of H_2S , could not be filtered due to colloidal iron formation on exposure to the atmosphere. They were processed directly.

For ^{32}Si studies, 500–3400-l water samples were collected in plastic swimming-pool-type tanks from the surface waters of Pavin lake and from rain, snow and waters from the neighbouring regions during 1975/1976. Two small box cores EM 40 and 43 were collected from the bottom of the anoxic layer during September 1975. In October 1978, two 20-cm-diameter gravity cores were collected using a modified Burke's (1968) corer. Core PL V was collected from a shallower depth (48 m) in the sediment underlying the oxygenated layer and core PL VI was collected in a water depth of 92 m, i.e. in the sediments under the anoxic layer. After siphoning out the fluid on top, all cores were sliced into several sections at the site. The wet densities were determined on aliquot samples whereas the bulk of the samples were dried at 105°C for 24 hr. and powdered in an agate mortar and used for radioisotope analyses.

2.2. Processing and analyses

For ^{210}Pb and ^{226}Ra isotopes in waters, the samples were acidified with HNO_3 to pH 1–2, stable Pb and Ba carriers were added and after homogenisation, BaSO_4 was precipitated with H_2SO_4 . Then $\text{Fe}(\text{OH})_3$ precipitation was car-

TABLE 1

^{210}Pb and ^{226}Ra in Pavin lake waters

No.	Sample	Depth (m)	^{210}Pb concentration (dpm/100 l)		Total	^{226}Ra (dpm/100 l)
			in particles* ¹	in water		
1	near shore (1975)	~0	9.4 ± 0.4	3.9 ± 0.4	13.3 ± 0.6	2.5 ± 0.5
2	near shore (1975)	~0	7.6 ± 0.5* ²	6.4 ± 0.6* ²	14.0 ± 0.8	—
3	mid-lake (1975)	~0	5.1 ± 0.3	3.8 ± 0.4	8.9 ± 0.5	3.3 ± 1.4
4	mid-lake (1978)	~0	—	—	14.5 ± 0.2	—
	mean surface water		7.3 ± 0.7* ³	3.9 ± 0.4* ³	12.7 ± 0.6* ⁴	2.9 ± 1.1
5	mid-lake	80	—	—	46.6 ± 0.5* ⁵	19.8 ± 1.6* ⁵

— = not analysed.

*¹Water samples were filtered through No. 113 and 0.45- μm Millipore[®] filter; the two filters were combined and processed for ^{210}Pb . Filtered water was processed for ^{210}Pb and ^{226}Ra .

*²Sample filtered through no. 113 only.

*³Average of 1 and 2.

*⁴Average of 1–4.

*⁵Total sample—no filtration was possible.

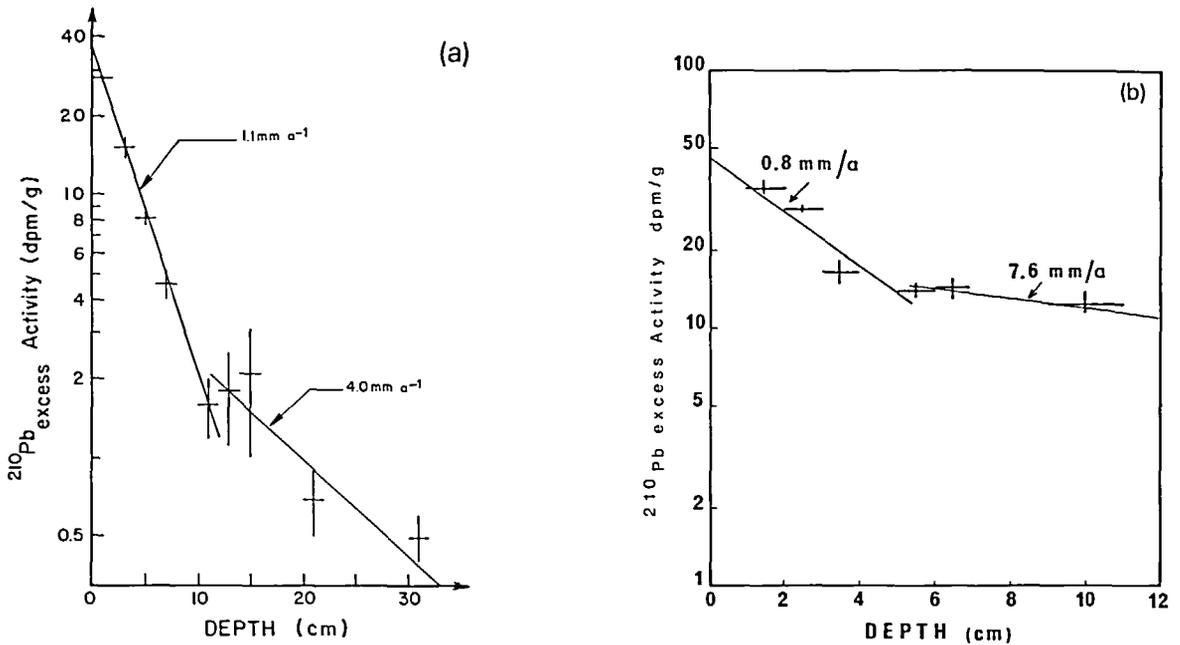


Fig. 1. Log of ²¹⁰Pb_{excess} activity v. depth for: (a) core PL V; and (b) core PL VI. Numbers indicated are accumulation rates.

TABLE II

³²Si in precipitation and waters from lake Pavin and surroundings

Sample	Collection date	Volume processed (10 ³ l)	Inherent SiO ₂ (mg l ⁻¹)	Net ³² P activity (cph)	³² Si	
					concentration (dpm/1000 l)	specific activity (dpm/kg SiO ₂)
Rain 1* ¹ (Thonon-les-Bains)	Jul./Aug. 1975	0.5	0.58	3.5	0.62 ± 0.08	-* ²
Rain 2 (Thonon-les-Bains)	Aug. 1975	0.86	0.13	7.1	0.46 ± 0.04	-* ²
Snow (Thonon-les-Bains)	Dec. 1975–Mar. 1976	1.58	0.18	2.3	0.07 ± 0.01	-* ²
Dranse* ³ (low water stage)	Feb. 1975	2.50	3.28	4.8	0.27 ± 0.03	82.3 ± 9.1
Dranse (high water stage)	May 1975	1.52	2.50	8.4	0.41 ± 0.05	164 ± 20
Rhue* ⁴ (low water stage)	Apr. 1975	2.76	21.3	4.3	0.24 ± 0.02	11.3 ± 0.9
Pavin lake (surface water)	Sep. 1975	3.40	14.48	4.3	0.14 ± 0.02	9.7 ± 1.4
Garonne* ⁵ (La Réole)	Feb. 1976	1.52	4.48	4.0	0.23 ± 0.03	51.3 ± 6.7

cph = counts per hour. Errors indicates for ³²Si data are 1σ counting statistics only.

*¹Thonon-les-Bains is located at 250 km east of lake Pavin, on the Geneva lake shore.

*²Due to the very low and highly varying Si contents of rain and snow, specific activities will have no meaning.

*³The Dranse river near Thonon-les-Bains flows through limestone.

*⁴The Rhue river near Pavin lake flows through basalts.

*⁵The Garonne river has a miscellaneous watershed.

ried out to scavenge both Pb and BaSO₄. The precipitate was then analysed in the laboratory for ²¹⁰Pb (Krishnaswami and Sarin, 1976) and ²²⁶Ra by Rn emanation methods (Bhat et al., 1974). In the case of sediment samples ~3 g of the powdered material were boiled in 6 M HCl (20 ml g⁻¹) three times and centrifuged. The leach along with distilled water washings were used for radiochemistry after the addition of the stable Pb carrier. Radiochemically pure PbSO₄ was beta assayed for the ingrowth of its daughter ²¹⁰Bi (Krishnaswami et al.,

1971). Particulates filtered from lake waters were processed in the same manner. For ³²Si measurements, pure SiO₂ was extracted from 50–100 g dry sediment by boiling with 2 M NaOH (Nijampurkar et al., 1983). In the case of large-volume water samples, the ³²Si was scavenged by Fe(OH)₃ precipitation after stable Si carrier addition (for waters with Si ≈ 1 ppm). The pure SiO₂, after 3–4 months of recovery, was measured for ³²Si via beta assay of its daughter ³²P activity following standard procedures (Kharkar et al., 1966; Nijampurkar and Somayajulu, 1974).

TABLE III

³²Si in Pavin lake sediments

Sample depth (cm)	SiO ₂ recovered (g)	Net ³² P activity (cph)	³² Si* (dpm/kg SiO ₂)
<i>Core EM 40:</i>			
0–15	38.2	(1) 3.3 ± 0.5 (2) 2.2 ± 1.0	8.2 ± 1.3 <u>8.5 ± 1.9</u> M = 8.4 ± 1.2
<i>Core EM 43:</i>			
0–5	8.1	1.5 ± 0.6	13.1 ± 5.3
5–10	10.8	2.1 ± 0.3	8.0 ± 1.2
10–15	9.8	(1) 2.3 ± 0.3 (2) 1.1 ± 0.6	7.5 ± 0.9 <u>7.8 ± 4.2</u> 7.7 ± 2.1
<i>Core PL VI:</i>			
10–11	15.1	(1) 3.2 ± 0.3 2.5 ± 0.8	11.2 ± 1.0 <u>18.2 ± 5.8</u> M = 14.7 ± 3.0
30–32	42.6	(1) 2.0 ± 0.3 (2) 2.5 ± 0.3	3.7 ± 0.5 <u>2.8 ± 0.3</u> M = 3.3 ± 0.3
40–42	34.9	2.2 ± 1.0	4.5 ± 2.1
60–62	27.5	1.3 ± 0.4	2.6 ± 0.8
70–72	34.2	(1) 2.5 ± 0.6 (2) 2.0 ± 0.2	4.4 ± 1.0 <u>4.3 ± 0.4</u> M = 4.4 ± 0.5
90–92	40.2	2.6 ± 0.7	2.1 ± 0.5

cph = counts per hour. (1) and (2) denote separate determinations of ³²P and *M* the weighted mean. Errors quoted are propagated 1σ counting statistics on ³²P measurements.

*Decay corrected to the date of collection.

3. Results

3.1. ²¹⁰Pb and ²²⁶Ra data

The ²¹⁰Pb concentrations of filtered and unfiltered lake water samples as well as that of particulates are given in Table I. In the case of ²²⁶Ra, only unfiltered samples were processed, the concentrations are also given in Table I.

The ²¹⁰Pb_{excess} activity v. depth plots for the two cores PL V and PL VI are shown in Fig. 1a

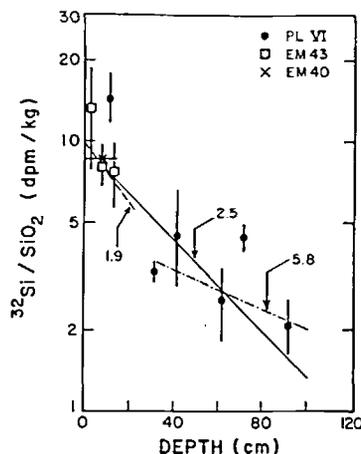


Fig. 2. Plot of log ³²Si/SiO₂ v. depth for all samples from the three cores analysed. Numbers indicated across best-fit lines are accumulation rates in units of a⁻¹. All data points yield 2.5 mm a⁻¹. For the top 20 cm the rate is 1.9 mm a⁻¹ and for the depth range 30–92 cm the rate is 5.8 mm a⁻¹. A break in the sedimentation rate at ~30 cm appears more reasonable. See Section 4.3 for discussion.

and b, respectively. It should be mentioned here that three samples per core were analysed for ^{226}Ra whose concentrations average ~ 1 dpm g^{-1} in the case of each core.

3.2. ^{32}Si data

^{32}Si concentrations in precipitation (rain and snow) near the Pavin lake region, in stream waters flowing through different geological terrains and in the surface waters of the lake are given in Table II. The ^{32}Si measurements performed on three cores from Pavin lake are given Table III. The same are plotted in Fig. 2.

4. Discussion

For clarity, ^{210}Pb and ^{226}Ra results and those of ^{32}Si are discussed separately.

4.1. ^{210}Pb and ^{226}Ra in lake waters

The total (dissolved + particulate) ^{210}Pb concentrations in the surface waters range from 8.9 to 14.5 dpm/100 l with a mean value of 12.7 ± 0.6 dpm/100 l out of which the particulates account for $\sim 60\%$; the mean particulate ^{210}Pb concentration is 7.3 ± 0.4 dpm/100 l. The ^{226}Ra content of surface water is 2.9 ± 1.1 dpm/100 l. The $^{210}\text{Pb}_{\text{dissolved}}/^{226}\text{Ra}$ ratio is ~ 1.3 in surface waters — this can be as high as 4.4 if we take the total ^{210}Pb instead of the dissolved part. For the deep water, only the $^{210}\text{Pb}_{\text{total}}$ (dissolved + particulate) measurement is available (Table I). The $^{210}\text{Pb}_{\text{total}}/^{226}\text{Ra}$ activity ratio is 2.4. The above inferences are based on the assumption that all the ^{226}Ra measured in the lake waters is in the dissolved form. This assumption does not appear unreasonable as most of the suspended phases of the lake waters comprise diatoms which have a low ^{226}Ra content (~ 1 dpm g^{-1}) and which deposit onto the lake floor, making the bulk density of the lake sediment 0.07 g cm^{-3} (Martin, 1985). Using the ^{210}Pb and ^{226}Ra data in Table I and from

knowledge of the volumes of the mixed (oxic) and deep (anoxic) layers (Martin, 1985), we calculate the ^{210}Pb and ^{226}Ra inventories of Pavin lake. These are $(4.6 \pm 0.1) \cdot 10^9$ dpm ^{210}Pb and $(1.5 \pm 0.2) \cdot 10^9$ dpm ^{226}Ra , which yield a mean $^{210}\text{Pb}/^{226}\text{Ra}$ ratio of ~ 3 for the lake water. In ocean waters, where ^{210}Pb - ^{226}Ra disequilibrium was established (Craig et al., 1973), it is seen that the $^{210}\text{Pb}/^{226}\text{Ra}$ activity ratios are generally greater than unity only in the mixed layer, which is due to atmospheric input of ^{210}Pb . Integrated over the entire oceanic water column, however, the $^{210}\text{Pb}/^{226}\text{Ra}$ ratio is < 1.0 (Somayajulu and Craig, 1976; Broecker and Peng, 1982). The excess ^{210}Pb over parental ^{226}Ra in the entire Pavin lake water column suggests that the former is supplied more than the latter. A quantitative explanation awaits more detailed measurements of ^{210}Pb and ^{226}Ra in various parts of the lake system.

4.2. Residence times of ^{210}Pb and ^{226}Ra

Now that the inventories of ^{210}Pb and ^{226}Ra in the lake waters are made, one can, assuming steady-state conditions, calculate the residence times of these nuclides in the lake. This, in principle, can be done in two ways: (1) from the knowledge of the input fluxes of these nuclides into the lake; and (2) by estimating the removal fluxes of the nuclides from the lake to its sediments. While carrying out the water balance studies, Martin (1985) noted that a significant input to the lake occurs via the underground lacustrine springs whose ^{210}Pb and ^{226}Ra concentrations are however not known. Therefore, we adopted the second method. In this study two sediment cores from Pavin lake, PLV from the shallower oxic layer and PLVI from the deep anoxic layer, have been dated. The accumulation rates for the top sections are 1.1 and 0.8 mm a^{-1} . These together with the earlier measurements (Krishnaswami et al., 1971; Martin, 1985) indicate that during the recent past (50–100 a) the average sediment

accumulation rate has been $\sim 1 \text{ mm a}^{-1}$ and that the extrapolated-to-surface ^{210}Pb activities of the Pavin sediments are $\sim 55 \text{ dpm g}^{-1}$. In the case of ^{226}Ra the mean concentration from several measurements is $\sim 1 \text{ dpm g}^{-1}$. Using these values and a bulk density of 0.07 g cm^{-3} the removal rates (dC/dt) of the two nuclides are calculated to be $0.39 \text{ dpm cm}^{-2} \text{ a}^{-1}$ ^{210}Pb and $7 \cdot 10^{-3} \text{ dpm cm}^{-2} \text{ a}^{-1}$ ^{226}Ra . The inventories (calculated using details given in Fig. 4) are 0.2 dpm l^{-1} , 1.8 dpm cm^{-2} ^{210}Pb and 0.07 dpm l^{-1} , 0.6 dpm cm^{-2} ^{226}Ra , respectively. Using the equation:

$$\tau = \frac{C}{dC/dt} \quad (1)$$

the calculated residence times (τ) are ~ 3 and ~ 86 a for ^{210}Pb and ^{226}Ra , respectively. If the dissolved inventory is considered the ^{210}Pb residence time will reduce to a mere ~ 1 a. Though very limited in number, the ^{210}Pb fall-out data from the Paris area are found to range from 0.2 to $0.7 \text{ dpm cm}^{-2} \text{ a}^{-1}$ (Thomas, 1988) which agrees well with the deposition rate of ^{210}Pb (dC/dt), indicating that the deduced residence time of ^{210}Pb is reasonable. Obviously a more detailed study is warranted to better understand the nuclides' behaviour in the lake system.

4.3. ^{210}Pb geochronology

The accumulation rates deduced using ^{210}Pb are not uniform with depth (Fig. 1); both cores show a change from a previous faster rate to a recent slower rate. Core PL V (water depth 48 m) yielded 4 mm a^{-1} slowing down to 1.1 mm a^{-1} compared to PL VI which yielded 7.6 mm a^{-1} slowing down to 0.8 mm a^{-1} . These accumulation rates are in good agreement with those determined for other lakes from different geographic locations using radiometric techniques (Krishnaswami et al., 1971; Koide et al., 1973; Robbins, 1978; Edgington et al., 1991). In general, the Pavin lake sediments which were depositing at rates of $4\text{--}10 \text{ mm a}^{-1}$

till $\sim 100\text{--}50$ a ago started accumulating more slowly after this time. The causes for such a lake's wide decrease can be due to: (1) sediment slump that would have occurred prior to ~ 100 a; (2) tree plantation in the catchment area during the middle of the last century; and (3) a change in the chemistry of the lake from a well-mixed to meromictic type as it is at present. Either one or all of the three causes could result in a decrease in the sedimentation rate (Martin, 1985).

4.4. ^{32}Si in waters from the Pavin lake area and other French sites

The ^{32}Si concentrations in rainwater are by far the highest, $0.54 \text{ dpm}/1000 \text{ l}$ (mean of two measurements, Table II) whereas the lowest concentrations of $0.07 \text{ dpm}/1000 \text{ l}$ is encountered in snow at the same latitude. The only difference between the locations is altitude and time of collection; rain was collected at an altitude of 380 m A.M.S.L. during July/August whereas snow was collected at 1800 m A.M.S.L. during December–March (Table II). Either snow is an inferior scavenger of aerosols compared to rain or the shorter (by 1420 m) air column available for snow scavenging made the difference, or there is a seasonality influence to the ^{32}Si concentrations in precipitation. It is assumed that rain and snow both account for the total annual atmospheric fallout of $\sim 100 \text{ cm}$ (on 50:50 basis). Using the concentrations in Table II, we compute the annual ^{32}Si fallout of $31 \cdot 10^{-6} \text{ dpm cm}^{-2}$ at the lake site (45°N), which falls in the range of $(17\text{--}100) \cdot 10^{-6} \text{ dpm cm}^{-2}$ reported for Indian stations at $10\text{--}30^\circ\text{N}$ (Lal et al., 1979).

Stream waters flowing through different geological terrains have about the same ^{32}Si content, viz. $0.23\text{--}0.41 \text{ dpm}/1000 \text{ l}$, with a mean value of $0.28 \text{ dpm}/1000 \text{ l}$. However, ^{32}Si specific activity varied significantly in the waters, which is due to their stable Si contents. Waters flowing through basaltic terrain have the highest Si and lowest $^{32}\text{Si}/\text{SiO}_2$ ratio while

waters draining limestone areas have the lowest Si and highest ³²Si/SiO₂ ratios (Table II). The Pavin lake surface waters have 0.14 dpm/1000 l ³²Si which is lower than any of the measurements reported in Table II with the exception of snow.

4.5. Model for ³²Si in Pavin lake

Now that waters from Pavin lake and environments which feed into it as well as the lake sediments have been analysed for ³²Si, a two-box model can be set up from which the missing ³²Si concentrations, for example as those of the anoxic deep layer and of the underground lacustrine springs which feed into it, can be estimated. These measurements will help in making the mass balance for ³²Si as well as in the understanding of its aqueous geochemistry.

We took the two-box model suggested by Martin (1985) to make a water balance and put in the biology component. In principle, the model is similar to that of Lal et al. (1960) which was used to explain the earliest ³²Si data in the Pacific Ocean.

We assume steady-state conditions and first-

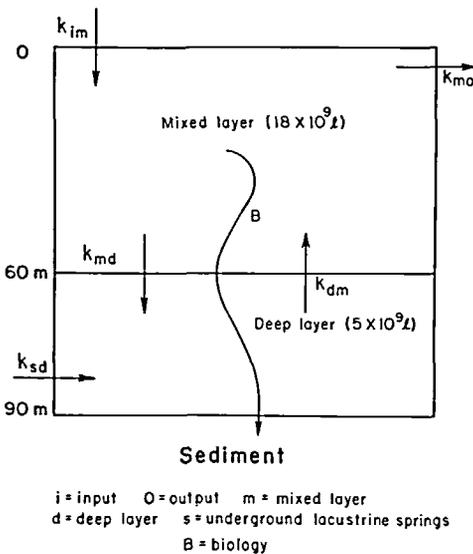


Fig. 3. A two-box model including biology for lake Pavin showing the steady-state input and output material fluxes. See Table IV and Sections 4.5 and 4.6 for discussion.

TABLE IV

Values of parameters used*1 in the model calculations

k (s ⁻¹)		C (dpm/1000 l)		Ck (dpm (1000 l) ⁻¹ s ⁻¹)	
parameter	value (×10 ⁻⁹)	parameter	value	parameter	value (×10 ⁻⁹)
k_{im}	2.9	C_i	0.24	$C_i k_{im}$	0.7
k_{md}	0.28	C_m	0.14	$C_m k_{md}$	0.04
k_{mo}	5.2	C_m	0.14	$C_m k_{mo}$	0.72
$k_B^{(*2)}$	3.6	C_m	0.14	$C_m k_B$	0.51
k_{sd}	8.0	C_{sd}	-		-
k_{dm}	9.0	C_d	-		-

— = to be determined.

*1 Obtained using data from Martin (1985) and Tables 2 and 3.

*2 Using the Si concentration of 2.5 · 10⁻⁴ mol l⁻¹ (Martin, 1985) and a deposition rate of 1 mm a⁻¹ and an area of 0.4 km² for the of the lake bottom, the equivalent volume of water (l) depleted of its Si (and ³²Si) by biological processes is deduced, from which k_B is obtained.

order rate constants and further that the residence time of ³²Si in the deep layer of the lake is small compared to its half-life so that there is no decay of ³²Si in the lake. The model with the input–output path-ways is shown in Fig. 3. The steady-state mass-balance equations for the top and bottom boxes are, respectively:

$$C_i k_{im} + C_d k_{dm} = C_m (k_{md} + k_{mo} + k_B) \quad (2)$$

$$C_s k_{sd} + C_m k_{md} = C_d (k_{dm} + \lambda) \quad (3)$$

where C represents the ³²Si concentration in units of dpm/1000 l; k is the rate constant; and λ is the decay constant of ³²Si (=0.0495 a⁻¹). The different rate constants together with the mass fluxes are given in Table IV. We proceed as follows: C_s is determined by substituting eq. 3 into eq. 2 after making $C_d = 0$ (as assumed above), which yields:

$$C_s = [C_m (K_{mo} + K_B) - C_i K_{im}] K_{sd}^{-1} \quad (4)$$

Plugging in the appropriate numbers from Table IV, C_s is calculated to be 0.07 dpm/1000 l. Considering the fact that a large amount of ³²Si enters the lake through subsurficial springs

(Martin, 1985) and that ^{32}Si in the surface layer is removed via diatom generation, the low value does not seem unreasonable. It is tempting to postulate that snow-melt waters which have the same ^{32}Si concentration as that deduced for deep water are indeed the source for the underground lacustrine springs. Now that C_s is known, C_d can be calculated using eq. 2 and the data from Table IV. It also turns out to be 0.07 dpm/1000 l, providing that the ^{32}Si concentration of the deep layer is mainly controlled by that of the underground lacustrine springs, C_s .

To calculate the residence time of ^{32}Si , the same procedure used in the case of ^{210}Pb and ^{226}Ra is followed. From the known volumes and ^{32}Si concentrations of the two layers, the lake inventory for ^{32}Si (C) is calculated: $2.9 \cdot 10^6$ dpm. The extrapolated-to-surface $^{32}\text{Si}/\text{SiO}_2$ ratio is ~ 10 dpm kg^{-1} in the lake sediments (Fig. 3) which yields a ^{32}Si deposition rate (dC/dt) of $3.1 \cdot 10^5$ dpm a^{-1} if we use a sedimentation rate of 1 mm a^{-1} . Using eq. 1, the ^{32}Si residence time is deduced to be ~ 10 a.

4.6. ^{32}Si in Pavin sediments

The EM cores were short, ~ 20 cm in length, and only a few measurements were possible. In core PL VI, ^{32}Si measurements could be made down to 92 cm and the data for all the cores are plotted in Fig. 2 to deduce the probable accumulation rate in the lake. This rate, depending on the data sets considered, varies from 1.9 to 5.8 mm a^{-1} . It appears that the most likely rate is 1.9 mm a^{-1} upto ~ 40 cm and 5.8 mm a^{-1} for the deeper part of the core (Fig. 2). The pattern of the ^{32}Si depth variation resembles that of ^{210}Pb in cores PL V and VI and so does the change in the accumulation rate (see Fig. 1a and b). The change in the sedimentation rate, from the ^{32}Si data, occurred around 200 a ago whereas the ^{210}Pb decay yields 50–100 a and the historical records suggest ~ 100 a (Martin, 1985). Considering the overall errors associ-

ated with the ^{32}Si data, we feel that a factor of ~ 2 difference is not unreasonable.

Since the Si and ^{32}Si contents of the surface and deep waters of the lake have been measured or deduced, the $^{32}\text{Si}/\text{SiO}_2$ ratios can now be calculated. They are 9.3 and 1.3 dpm kg^{-1} for the oxic surface waters and the deep anoxic waters, respectively. The extrapolated-to-surface $^{32}\text{Si}/\text{SiO}_2$ in the sediments (10 dpm kg^{-1}), as expected, agrees well with the surface water value, indicating that diatom formation takes place in the surface waters. The low deep water value indicates the dominance of the underground spring waters whose model-based ^{32}Si concentration is almost identical to that of the deep waters, viz. 0.07 dpm/1000 l. Any diatom dissolution in large amounts on the lake floor would have increased the $^{32}\text{Si}/\text{SiO}_2$ ratio of the deep waters and consequently the residence time of ^{32}Si added to Pavin lake is deposited on to the lake floor where it decays.

The ^{32}Si inventory in Pavin sediments yields $1.4 \cdot 10^{-2}$ dpm cm^{-2} which is almost identical to that expected from the atmospheric fallout, viz. $1.1 \cdot 10^{-2}$ dpm cm^{-2} within the errors associated with the measurements. This probably suggests that snow-melt waters are not contributing much to the ^{32}Si fallout in the lake.

5. Conclusions

The ^{210}Pb , ^{32}Si and ^{226}Ra isotopes in Pavin lake have residence times of ~ 1 , ~ 10 and ~ 80 a, respectively. In the case of ^{32}Si , where fallout measurements are available from the lake region, the inventory based on fallout data is present in the lake sediments were most of it decays. A two-box model adequately accounting for biology explains the ^{32}Si behaviour in the lake. It is shown that the ^{32}Si in the anoxic deep layer is controlled not by the overhead input but by the underground lacustrine springs. The deposition rate of the lake sediments based on ^{210}Pb and ^{32}Si indicates a decrease by factors of ~ 5 which occurred about a century ago.

In a way lake Pavin acts as a rain gauge for atmospherically derived nuclides and therefore can be used to understand their geochemistry under redox conditions.

Acknowledgements

The authors are thankful to Dr. J.D. Burton and an anonymous reviewer for their critical reviews which served to improve the manuscript significantly.

References

- Bhat, S.G., Krishnaswami, S. and Rama, 1974. Radon concentrations of air over the eastern Arabian Sea. *Proc. Indian Acad. Sci.*, 80: 109–116.
- Broecker, W.S. and Peng, T.H., 1982. *Tracers in the Sea*. LDGO Press, New York, N.Y., 690 pp.
- Burke, J.G., 1968. A sediment coring device of 21 cm diameter with sphincter core retainer. *Limnol. Oceanogr.*, 13: 714–718.
- Craig, H., Krishnaswami, S. and Somayajulu, B.L.K., 1973. ^{210}Pb – ^{226}Ra : radioactive disequilibrium in the deep sea. *Earth Planet Sci. Lett.*, 17: 295–304.
- Edgington, D.N., Val Klump, J. Robbins, J.A., Kusner, Y.S., Pampura, V.D. and Sandimirov, I.V., 1991. Sedimentation rates, residence times and radionuclide inventories in Lake Baikal from ^{137}Cs and ^{210}Pb in sediment cores. *Nature (London)*, 350: 601–604.
- Kharkar, D.P., Nijampurkar, V.N. and Lal, D., 1966. The global fallout of ^{32}Si produced by cosmic rays. *Geochim. Cosmochim. Acta*, 30: 621–631.
- Koide, M., Bruland, K.W. and Goldberg, E.D., 1973. Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. *Geochim. Cosmochim. Acta*, 37: 1171–1187.
- Krishnaswami, S. and Lal, D., 1978. Radionuclide limnology. In: A. Lerman (Editor), *Lakes: Chemistry, Geology and Physics*. Springer, Berlin, pp. 153–177.
- Krishnaswami, S. and Sarin, M.M., 1976. The simultaneous determination of Th, Pu, Ra isotopes, and ^{210}Pb , ^{55}Fe , ^{32}Si and ^{14}C in marine suspended phases. *Anal. Chim. Acta*, 83: 143–156.
- Krishnaswami, S., Lal, D., Martin, J.M. and Meybeck, M., 1971. Geochronology of lake sediments. *Earth Planet. Sci. Lett.*, 11: 407–414.
- Lal, D. and Somayajulu, B.L.K., 1984. Some aspects of the geochemistry of silicon isotopes. *Tectonophysics*, 105: 383–397.
- Lal, D., Goldberg, E.D. and Koide, M., 1960. Cosmic ray produced ^{32}Si in nature. *Science*, 131, 332–337.
- Lal, D., Nijampurkar, V.N., Rajagopalan, G. and Somayajulu, B.L.K., 1979. Annual fall out of ^{32}Si , ^{210}Pb , ^{22}Na , ^{35}S and ^7Be in rains in India. *Proc. Indian Acad. Sci.*, 88A: 29–40.
- Lerman, A. (Editor), 1978. *Lakes: Chemistry, Geology and Physics*. Springer, Berlin, 363 pp.
- Martin, J.M., 1985. The Pavin crater lake. In: W. Stumm (Editor), *Chemical Processes in Lakes*. Wiley, New York, N.Y., pp. 169–188.
- Meybeck, M., Martin, J.M. and Olive, P., 1975. Géochimie des eaux et des sédiments de quelques lacs volcaniques du Massif-Central. *Verh. Int. Ver. Limnol.*, 19: 1150.
- Nijampurkar, V.N. and Somayajulu, B.L.K., 1974. An improved method of silicon-32 measurement in groundwaters. *Proc. Indian Acad. Sci.*, 80A: 289–298.
- Nijampurkar, V.N., Martin, J.M. and Meybeck, M., 1983. Silicon-32 as a tool for studying silicon behaviour in estuaries. *Limnol. Oceanogr.*, 28: 1237–1242.
- Robbins, J.A., 1978. Geochemical and geophysical applications of radioactive lead. In: J.O. Nriagu (Editor), *The Biogeochemistry of Lead in the Environment*. Elsevier, Amsterdam, pp. 285–393.
- Schell, W.R., 1982. Dating recent (200 years) events in sediments from lakes, estuaries and deep ocean environments using lead-210. In: L. Currie (Editor), *Nuclear and Chemical Dating Techniques—Interpreting the Environmental Record*. Am. Chem. Soc., Washington, D.C., Symp. Ser., 176, pp. 331–361.
- Somayajulu, B.L.K. and Craig, H., 1976. Particulate and soluble ^{210}Pb activities in the deep sea. *Earth Planet. Sci. Lett.*, 32: 268–276.
- Somayajulu, B.L.K., Rengarajan, R., Lal, D., Weiss, R.F. and Craig, H., 1987. GEOSECS Atlantic ^{32}Si profiles. *Earth Planet. Sci. Lett.*, 85: 329–342.
- Somayajulu, B.L.K., Rengarajan, R., Lal, D. and Craig, H., 1991. GEOSECS Pacific and Indian Ocean ^{32}Si profiles. *Earth Planet. Sci. Lett.*, 107: 197–216.
- Thomas, A.J., 1988. *Géochimie des radioéléments naturels et artificiels—application a l'étude de l'interface continent-océan*, Ph.D. Thesis, Pierre et Marie Curie University, Paris, 409 pp.
- Turekian, K.K., Nozaki, Y. and Benninger, L., 1977. Geochemistry of atmospheric radon and radon products. *Ann. Rev. Earth Planet. Sci.*, 5: 227–255.
- Volchok, H.L., Feiner, M., Simpson, M.J., Broecker, W.S., Noshkin, V., Bowen, V.T. and Willis, E., 1970. Ocean fallout: The Crater Lake experiment. *J. Geophys. Res.*, 75: 1084–1091.