

COSMIC RAY PRODUCED SILICON-32 IN NEAR-COASTAL WATERS

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ABSTRACT

The specific activity of Silicon-32 is measured in near-coastal sea-waters using an *in situ* method for the extraction of dissolved silica. The results are discussed in relation to the input of Si^{32} at the surface *via* rains, the expected variation in its concentrations due to continental run-off and influx of open ocean surface waters. The experimental results clearly demonstrate the usefulness of Si^{32} as a tracer for the study of the vertical structure of the ocean in the upper layers, and of seasonal variations in the types of waters entering in the coastal regions.

1. INTRODUCTION

It has been discussed earlier that Si^{32} (a beta-emitter with a half-life of about 500 years) which is continuously produced by cosmic rays in the atmosphere and introduced into the marine environments *via* rains should form an excellent tracer for studying the nature of large-scale circulation in the oceans.^{1, 2} However, it becomes necessary to process sea-water samples of the order of 10–50 tons to measure the Si^{32} activity, despite the fact that one can measure its activity at extremely low levels by milking and counting its daughter nucleide, P^{32} . Because of this rather large sample requirement for an analysis, most of the measurements of Si^{32} in the literature refer to the analysis of siliceous sponges,^{3, 4} which form a natural agency for concentrating silicon from sea-water. This approach, though very convenient, does not allow studies of wide scale oceanic phenomena since sponges usually grow at shallow depths.

Recently a nylon reinforced rubber-bag water sampler was designed by Schink⁵ which permits one to bring on board the ship samples of 50–100 tons of sea-water. Using this sampler Schink measured the Si^{32} concentrations of a few samples from the Pacific Ocean. However, this technique

involves elaborate ship-board operations and is rather inconvenient for routine measurements.

In this paper, we discuss the experiments carried out in which dissolved silicon was extracted from sea-water using an *in situ* extraction method developed by Lal *et al.*⁶ in which the sea-water is allowed to flow freely through ferric-hydroxide suspended in a matrix form on natural spongin fibres. The results of $\text{Si}^{32}/\text{Si}^{28}$ ratios in several near-coastal water samples are presented.

2. EXPERIMENTAL PROCEDURES

Natural sponges were obtained in bulk from the sponge fishing companies of Greece and Florida. Initial cleansing of the sponges and the preparation of the ferric-hydroxide matrix were done essentially according to the procedures discussed by Lal *et al.*⁶

In the case of the experiments carried out off the coasts of Bombay and Mandapam, we used ordinary perforated steel samplers containing about 2–3 kg. of spongin matrix; these samplers were towed through surface sea-waters by small motor launches (Naval ship I.N.S. Khukri in the case of sample B 3) at a speed of about 3 knots for a period of 8–10 hours.

In the case of the surface sample from 100 miles off the San Diego coast, SD_1 , we placed the sponge matrix in a perforated stainless steel sampler which was left attached to a buoy for a period of 10 hours. Because of the movement of the buoy, water flows continuously through the samplers. The amount of silica picked up was about half of the saturation capacity of the matrix in as much as surface waters which usually have extremely low concentration of silica. This experiment was carried out during one of the cruises of the oceanographic vessel R/V Agassiz.

At all the sampling sites, sea-water samples of 1 litre volume were collected in poly-bottles for the determination of stable silicon.⁷

The silicon picked up by the matrix was extracted by treating it with hydrochloric acid followed by a dehydration step.⁶ The purification of crude silica and milking of P^{32} was carried out according to the procedure described by Kharkar *et al.*⁸ Reference is made here of a monograph on radiochemistry of silicon by Schink.⁹ The overall chemical efficiencies for milking P^{32} were usually around 80 per cent.

Most of the samples were counted with 2π -gas-flow type Geiger counters¹⁰; the counting efficiency for P^{32} beta-radiation was *ca.* 30 per cent and the background was 2–3.5 counts per hour (c.p.h.). Some of the samples

were counted on a 4π beta counter¹¹; counting efficiency—68 per cent ; background—5 c.p.h.

3. RESULTS

The pick-up of SiO_2 from sea-water varied between 0.1 and 0.5 per cent of the matrix on a dry weight basis depending on the silica concentration of the sea-water; the amount of ferric-hydroxide deposited in the sponge matrix was about 15 per cent by weight. As seen from Table I, the amount of silicon extracted corresponds to about 20–400 tons of water. The observed P^{32} activities in individual samples varied between 2–6 c.p.h. Despite the low activities observed the measurements are considered to be reliable because the net activities are based on the observed decay of P^{32} activity of short half-life (14 days) (see Figs. 1 and 2). Based on a least square analysis, the net activities (above background and any contamination present; Figs. 1 and 2) have been deduced in each case and the results are given in Table II, both in terms of Si^{32} dpm (disintegrations per minute) per kilogram of SiO_2 (i.e., specific activity of Si^{32}) and dpm per ton of sea-water (absolute concentration).

In order to check on the results, all samples were remilked; these results are also given Table II. As a further check, the three Bombay samples B1, B2, B3 were combined: the net observed activity of P^{32} , 5.3 ± 0.6 c.p.h. corresponds to an average value of 11 ± 2 dpm/kg. SiO_2 . Later, this combined silica was mixed with all the other samples and the specific activity of the total sample was found to be 12.3 ± 2.1 dpm/kg. SiO_2 . Considering the data in Table II on the specific activities in individual samples, we find that these results are in excellent agreement giving credence to the values measured.

4. DISCUSSION OF RESULTS

From an analysis of the data in Tables I, II, though limited, the following features are clear:

1. The surface sea-waters have both higher and lower Si^{32} specific activities, compared to the values obtained for the siliceous sponges collected from the same region (Table II). Several siliceous sponges collected from around the same region essentially gave identical specific activities⁴ implying that the siliceous sponges give a mean specific activity of Si^{32} averaged over their lifetimes which may be of the order of decades.

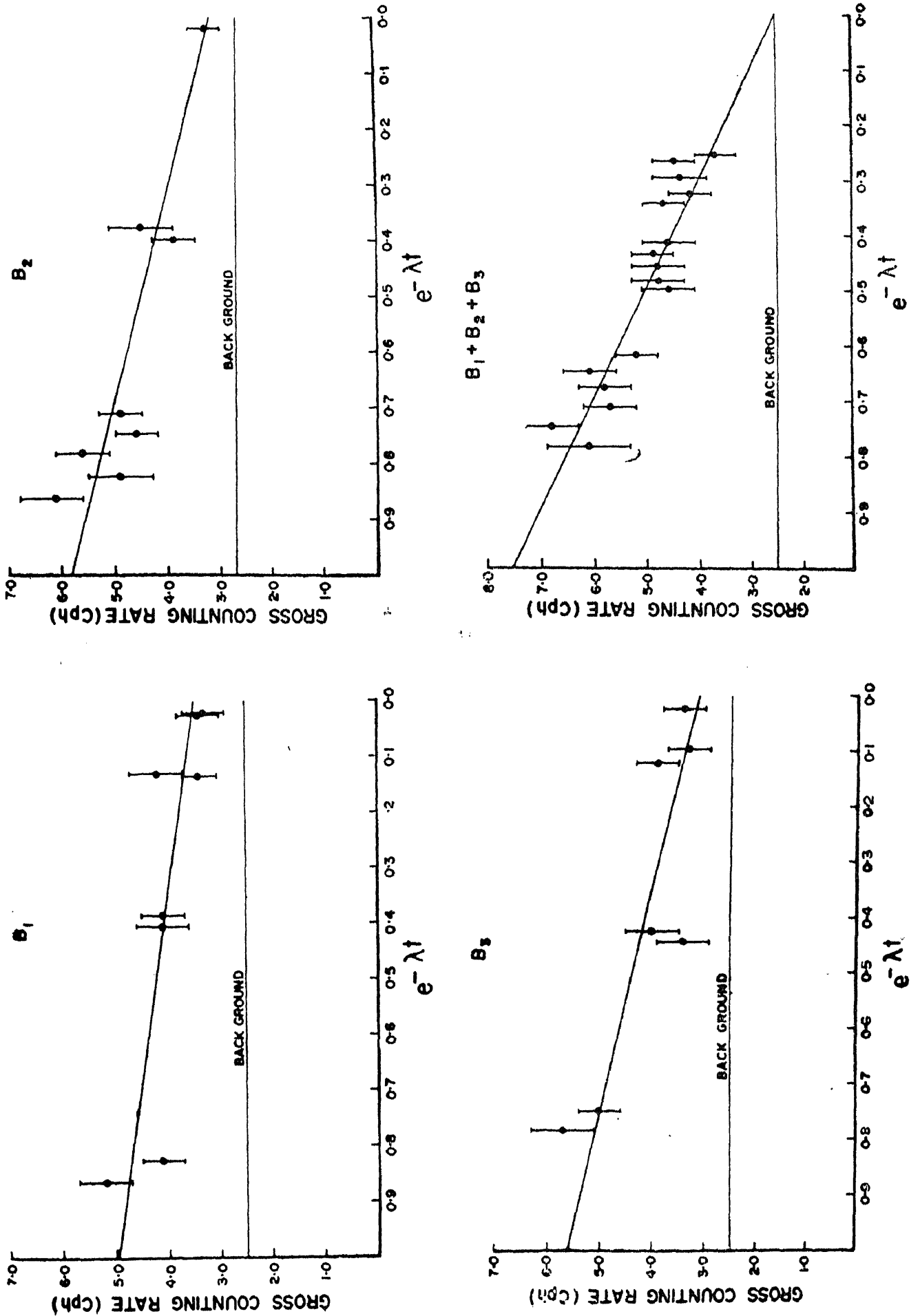


FIG. 1. Observed decay plots of P^{32} activities milked from Bombay samples B_1 , B_2 , B_3 and the total sample $B_1 + B_2 + B_3$.

TABLE I

Relevant details on samples studied for Si^{32} activity

Code No.	Nature of the sample	Location (Lat., Long.)	Depth (meters)	Date of collection	Stable Si concentration in water (mg. SiO_2 /liter)	Weight of SiO_2 extracted (gm.)	Equivalent tons of water
B ₁	Sea-water	Bombay (19°N, 74°E)	Surface	30th November 1963	0.79	19.0	24.0
B ₂	"	"	"	2nd April 1964	0.46	15.0	32.0
B ₃	"	"	"	27th May 1964	0.13	8.3	64.0
TF 52	Siliceous sponge	"	0-10	June 1964	..	28	..
M ₁	Sea-water	Gulf of Mannar, Mandapam (9° 10' N, 79° 09' E)	Surface	3rd January 1963	0.40	140	400
M ₂	"	"	"	10th December 1963	0.35	10	29.0
M ₃	"	"	"	1st February to 6th June 1964	0.45	13.1	29.0
TF 1	Siliceous sponge	"	0-10	April 1962	..	95	..
TF 11	Plankton (net collection)	"	Surface	"	0.4	5.9	15.0
SD ₁	Sea-water	San Diego, California (32° 57' N, 127° 05' W)	Surface	10th November 1966	0.03	3.3	110.0
S ₁	Siliceous sponge	"	300	"	..	45.0	..

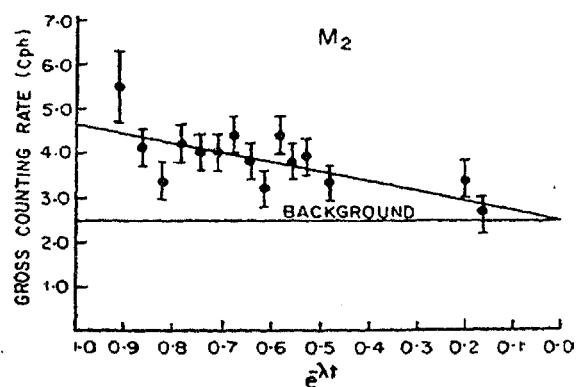
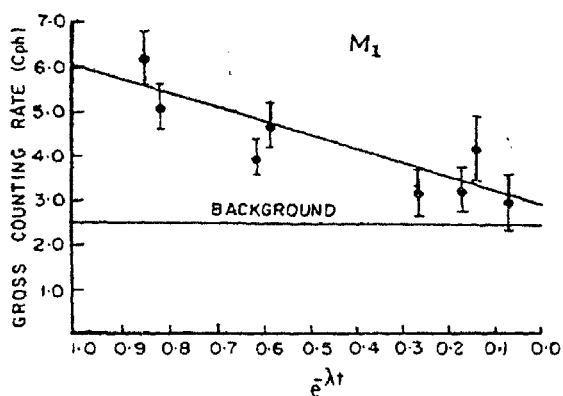
FIG. 2. Observed decay plots of P^{32} activities milked from Mandapam samples M₁ and M₂.

TABLE II

Si³² concentrations and Si³²/Si²⁸ ratios in near coastal waters

Sample code No.	Net activity* of P ³² (counts per hour)	Si ³² -concentration		Reference
		Specific activity (dpm/kg. SiO ₂)	Absolute concentration dpm/10 ³ tons of water	
BOMBAY:				
B ₁	.. (a) 1.4±0.3 (b) 5.2±0.5	11.6± 1.9	9.2±1.5	This work
B ₂	.. (a) 2.6±0.5 (b) 1.8±0.4	11.5± 2.2	5.3±1.0	do.
B ₃	.. (a) 2.5±0.5 (b) 3.2±0.4	41.6± 6.9	5.5±1.0	do.
TF 52 (Sponge)	.. 6.7±0.5	19.3±1.5	..	do.
MANDAPAM:				
M ₁	.. (a) 3.2±0.6 (b) 3.6±0.6	3.1± 0.4	1.3±0.2	6
M ₂	.. (a) 2.9±0.4 (b) 1.9±0.6	20.7± 4.4	6.9±1.5	This work
M ₃	.. (a) 2.2±0.5 (b) 1.7±0.5	13.8± 3.4	6.1±1.5	do.
TF 1 (Sponge)	.. (a) 7.8±1.1 (b) 9.2±1.8	7.8± 2.0	..	3
TF 11 (Plankton)	.. 2.1±0.8	43.5±16.0	17.4±6.4	3
SAN DIEGO:				
SD ₁	.. (a) 4.6±0.7 (b) 2.3±0.6	78 ±11	2.5±0.4	This work
S ₁ (Sponge)	.. (a) 7.4±0.7 (b) 3.9±0.6	12.7± 3.2	..	do.

* (a) and (b) refer to the two results based on separate milkings of P³².

2. The absolute concentration of Si³² in surface sea-waters in general is two to three orders of magnitude lower than that of rain-water (Table III).

TABLE III

Approximate range of concentrations of Silicon-32 in natural waters

Type of Natural water	Si ³² dpm/1000 l.	Si ³² dpm/kg. SiO ₂	Reference
Rain	.. 0.1 -1.0	..*	8
River	.. 0.1	5-10	12
Sea-water:			
(i) Surface	.. 0.001-0.01	3-80	This work†
(ii) Mixed layer (0-500 m)	4-84	4

* The concentration of stable silicon in rain-water is extremely low and hence the specific activity of Si³² in rains can be very high.

† The only other measurement is due to Schrink⁵ who measured surface waters off Hawaii; 12 ± 4 dpm/1,000 tons corresponding to specific activity of 99 ± 32 dpm/kg. SiO₂.

The specific activity of Si³² in surface sea-waters and river-waters is of the same order (Table III). This, however, is fortuitous since the physical processes operative, as well as the stable silica concentrations are very different in the two cases.

3. High values of Si³² specific activity are observed in the case of two samples collected 100 miles off the coast (B₃ and SD₁), and for the plankton sample, TF 11. These observations can be understood in terms of direct input of Si³² *via* rains in surface waters (which have low stable silicon concentrations; Tables I and II) and slow mixing.

4. During the south-west monsoon (May-October), open ocean-waters enter the Gulf of Mannar and the Palk Bay and a goodly 90 cm. of rainfall occurs¹⁵ in these areas during the subsequent two months period (Nov.-December). Both high absolute concentration and specific activity of Si³² are observed in the samples collected during this period (samples M₂ and M₃, *see* Table I), quite consistent with expectations.

5. Though the number of measurements are few it seems worth noting that the lowest Si³² absolute concentration as well as specific activity observed is in the case of the Mandapam sample M₁ (Table II). This sample was collected during a period when it is known from the oceanographic

observations that there is considerable influx of river-waters to the Gulf of Mannar, Mandapam and Palk Bay areas, resulting in low salinity.¹³ This phenomenon bears relation to the north-east monsoon. River-waters have high concentrations of silica and consequently specific activity of Si^{32} is low (Table III). Further dissolved silicon in river is quickly precipitated after mixing with sea-water,¹⁴ and therefore this may be the reason for the low concentration and specific activity for sample M_1 .

The above observations highlight the large seasonal variations that exist in coastal waters and it would be of interest to see the magnitude of such variations in the open-ocean waters.

It has been discussed¹ that in view of the biological removal of silicon from the surface waters which removes both Si^{28} and Si^{32} , it is instructive to consider the specific activities rather than the absolute concentrations. Further, considering typical mixing times in the oceans, one expects the specific activities in the surface layer be about a factor of two higher than the deep waters, based on a two-box model calculation.¹ This factor remains essentially unchanged even if more complex models¹⁶ are considered which involve several zones of slow mixing in the upper layers, as long as both the biological removal and vertical mixing occur at a constant rate. The data in Table II, however, do not support such model calculations; variations in the specific activity of Si^{32} seem to occur over factors of 25 implying seasonal character of both Si^{32} input *via* rains and biological removal of silica from surface layers.

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