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Paradox lost: silicon 32 and the global ocean silica cycle

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Abstract

The ³²Si Paradox is that the GEOSECS measurements of ³²Si specific activity in silica collected on ferric hydroxide-coated fibers are essentially uniform throughout the deep water of the global oceans [Somayajulu et al., *Earth Planet. Sci. Lett.* 85 (1987) 329–342; 107 (1991) 197–216]. Peng, Maier-Reimer, and Broecker have argued that ³²Si specific activities in Indian and Pacific deep water should be 3–5 times lower than in the deep Atlantic, because the dissolved SiO₂ concentrations are higher than in the Atlantic by this factor, and because cosmogenic ³²Si should be essentially confined to the ocean basins in which it falls due to its short half-life relative to mixing times for water interchange between the oceans. Thus these authors proposed that the entire GEOSECS ³²Si data set “may be flawed”. The resolution of the ³²Si Paradox is straightforward. Silica collected on the acrilan fibers is a two-phase mixture of biogenic particulate SiO₂ (opaline tests of diatoms and radiolaria) and silica scavenged chemically from dissolved SiO₂ in ocean water. Particulate silica is the high-activity component in this mixture, and dissolved SiO₂ is the low-activity end-member. Thus the mixing trajectories on ‘Cornucopia plots’ of specific activity vs. reciprocal SiO₂ recovered weights overlap in specific-activity range, regardless of the different concentrations and specific activities of dissolved silica in the deep waters. The specific activities of dissolved SiO₂ in the Pacific, Indian, and Atlantic oceans, as deciphered from the two-component total activity data, are ~0, 2.6, and 4.5 dpm/kg SiO₂. The atmospheric production rate of ³²Si has been calculated and is found to be 0.72 atoms/m² s. This value is much lower than in previous calculations, which were based on the Lal and Peters plots of stratospheric fallout that incorrectly use geomagnetic latitude for scaling the fallout patterns. Correcting these curves to scale by geographic latitude, which controls the stratospheric ‘dumping’ pattern, we show that the ³²Si concentrations in Indian rains represent the total fallout from both stratosphere and troposphere, rather than only tropospheric fallout as was previously assumed. The new value of the atmospheric production rate is consistent with the low activities of the dissolved silica in the three oceans, which are modulated to some extent by radioactive decay of ³²Si during the sequestering of particulate silica in sediments before regeneration in bottom waters. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Measurements of the cosmogenic nuclide ³²Si (mean life ≈ 202 years [2]) were made in seawater profiles during the GEOSECS program, in

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an attempt to establish the deep-water specific activity variations throughout the world oceans. From previous analyses of siliceous sponges and biogenic deposits, the specific activity of ^{32}Si in surface waters was known to be so low that literally tons of water would have to be processed to obtain enough ^{32}Si for reliable counting measurements. Thus 20 kg of ferric hydroxide-coated acrilan fibers contained in open-mesh bags were suspended for 8 h at each depth on the hydrographic wire to scavenge dissolved silica at the desired profile depths [1,2]. Silica recovered from the fibers by incineration and dissolution was stored for ingrowth and counting of the daughter isotope ^{32}P : together with the recovered amounts of silica these data were used to calculate the specific activities of ^{32}Si in the recovered silica samples.

The reported ^{32}Si specific activities [1,2] are invariant with dissolved silica concentrations throughout the Atlantic, Indian, and Pacific deep waters, in marked contrast with the better-known cosmogenic isotope ^{14}C , in which deep-water specific activity varies inversely with dissolved ΣCO_2 concentration because of particulate input of surface carbon by in situ oxidation and dissolution in deep waters [3]. Peng et al. [4] have thus argued that because the dissolved silica concentrations in Pacific and Indian deep waters are some 3–5 times greater than in the Atlantic, the observed ^{32}Si specific activities should be correspondingly lower by about the same factor, given that ^{32}Si is injected rather uniformly into the surface waters from the atmosphere and, because of its short half-life, is effectively confined to the deep waters of the individual oceans in which it enters the sea. This is the ^{32}Si Paradox, and it is on this basis that Peng et al. suggested that the entire ^{32}Si data set from the GEOSECS expeditions “may be flawed”.

In this paper we report the results of a study of the ^{32}Si GEOSECS data focused on this question. We show that the GEOSECS measurements are not, in fact, specific activities of dissolved silica in the oceans: instead the silica captured by the acrilan fibers is a mixture of dissolved silica and biogenic particulate silica.

2. Pacific Ocean ^{32}Si specific activities

Although the ^{32}Si specific activities are totally uncorrelated with dissolved silica concentrations, both within the Pacific itself and in the oceans world-wide, they are in fact well-correlated with the actual amounts of silica recovered from the acrilan fiber samples. In Fig. 1 the measured specific activities are plotted against the reciprocal of the recovered SiO_2 amounts (grams) for the subsurface Pacific samples. One sees that there is a well-defined linear correlation which forms a conical envelope extending from the origin and widening progressively at higher specific activities (lower SiO_2 recoveries). Fig. 1 shows therefore that the recovered silica is a two-component mixture in which there is a proportionally increasing symmetrical scatter of the data with increasing specific activity. It is clear that the components are two different phases of silica because if only dissolved silica had been recovered the specific activities would be correlated with dissolved SiO_2 concentrations in the ambient waters.

Another indication that the recovered silica is a two-phase mixture is given by the relationship of recovered silica to the actual dissolved SiO_2 in the ambient waters. A plot of recovered SiO_2 vs. dissolved SiO_2 concentration for all the GEOSECS samples (not shown) is a complete scatter diagram, so that the recovered SiO_2 is totally uncorrelated with ambient dissolved SiO_2 . If the fibers were collecting only dissolved silica, then since the immersion times are essentially uniform (~ 8 h) one would expect a correlation of recovered SiO_2 with dissolved SiO_2 because of the large range of SiO_2 concentration in the waters (a factor of 50 in subsurface waters, and 400 in all waters).

Fig. 1 thus demonstrates that the measured ^{32}Si specific activities are consistent with two-phase silica mixtures containing: (1) a high specific activity component of low concentration on the fibers, and (2) a low specific activity component of high concentration on the fibers. The low activity component cannot be airborne quartz – which contains no ^{32}Si – because the amounts required (up to 80% of the recovered silica in the lowest activity samples) are far too high. Honjo et al. [5]

found that in sediment traps deployed at 15°N in the Pacific, the ‘clay’ to opal ratios at 1, 2.8, 4.3, and 5.6 km depth were 33%, 13%, 20%, and 19%. Particulate silica in Atlantic surface waters has high specific activities (mean = 40, range = 20–60 dpm/kg SiO₂, $n=4$ [1]) and thus biogenic particulate silica is clearly the high activity end-member. It might be thought that the particulates in these samples are actually derived from trapping of surface water particulates on the fibers during lowering or recovery of the deep samplers, but this is not the case. The fiber packets were enclosed in large canvas Niskin bags during the descent of the hydrographic wire, which were opened at depth with a messenger for the soaking and flushing period, and closed again by a second messenger before the ascent, thus ensuring that all recovered silica, both dissolved and particulate, was derived from the depths at which the bags were opened (see [1] for details).

The two components in Fig. 1 are therefore

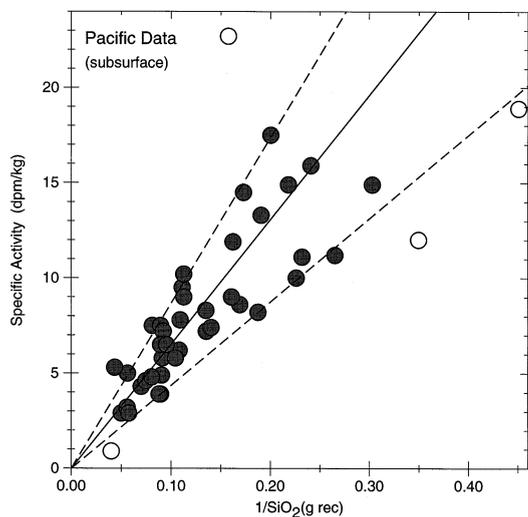


Fig. 1. Cornucopia plot of the ³²Si specific activities vs. reciprocal weights of recovered SiO₂ for the subsurface GEOSECS Pacific samples. The dashed lines represent a ±33% variation around the mean mixing trajectory between particulate and dissolved SiO₂ (solid line). All three lines are addition vectors for adding dissolved SiO₂ to constant amounts of recovered particulate silica. Open circles: data not used in the fit. The intercept is the nominal specific activity of dissolved silica in the Pacific, which is statistically zero (±0.08 dpm/kg). The slope of the median line is 0.065 dpm.

dissolved SiO₂ and particulate silica, both of which will have been collected on the acrilan fibers during the passage of seawater through the bags. The specific activity of the total recovered silica is $A_T = \lambda N_T^*/N_T$ where the asterisk identifies the recovered ³²Si amount, and $N_T A_T = [N_S A_S + N_P A_P]$, where A is specific activity (dpm/kg SiO₂), N is the recovered amount of silica (grams), and the subscripts T, S, and P refer to total silica, silica in solution, and biogenic particulate silica. The low specific activity component is the dissolved silica, and the high specific activity component is the particulate biogenic silica. In Fig. 1 the best-fit slope through the origin is $\lambda N_T^* = 0.065$ dpm, the mean activity of total recovered ³²Si in the samples. Thus the line corresponds to a histogram of λN_T^* , and the actual histogram (not shown) is close to a normal distribution with a standard deviation of ±33% (shown by the two dashed lines in Fig. 1 enclosing the envelope of the data). The 1σ statistical counting errors in the individual measurements ($n=86$) range from 10 to 51%, with a mean of $25.6 \pm 9\%$ [2], although about half of the samples were counted twice which reduces the individual errors. The observed range of ±33% is therefore consistent with the counting statistics, but also includes variations in the amounts and activities of SiO₂ recovered on the fibers.

3. The two-component mixing model

The specific activity of the silica recovered on the fibers is given by:

$$A_T = A_S + N_P(A_P - A_S)/N_T \quad (1)$$

in which the low activity component (the intercept) is A_S , the specific activity of dissolved SiO₂. The median line through the data in Fig. 1 is an addition vector for adding dissolved silica to any point on this line at constant particulate silica content, for constant specific activities A_P and A_S . Of course the actual trajectory from such a point to the origin will be a convex-up curve representing small zigzags through the diagram as both dissolved and particulate silica are

added. The horizontal spread of the data along the x -axis reflects: (1) variations in the amount of particulate silica collected, (2) variations in the amount of fibers (perhaps $\pm 10\%$) used in the samplers, and (3) losses of particulate material during rinsing of the fibers prior to silicate extraction. The first two of these effects are random and will have produced approximately symmetrical variations about the median line. That is, at $A_T = 16$ dpm/kg and $N_T = 4.0$ g, the horizontal spread across the data envelope is $N_T = 2.7$ – 5.5 g, or $\pm 35\%$ about the median line, and this percentage spread is present all along the median line. Of course in the plot the data envelope itself is asymmetrical across the median line because the reciprocal of N_T is plotted. The vertical spread of the data envelope is consistent with symmetrical counting errors that scale roughly with the square root of the activities and amount to $\sim \pm 33\%$ in the range of the data. We call Fig. 1 a ‘Cornucopia plot’, in which random variations in the variables (here counting errors and SiO_2 recovery fluctuations) introduce roughly symmetrical spreads on both axes and from which many good things emerge.

The Pacific Ocean dissolved SiO_2 end-member has a statistical specific activity close to zero (Fig. 1). The least-squares two-parameter fit gives an intercept of -0.024 ± 0.08 dpm/kg SiO_2 , and a slope of 0.0654 ± 0.0005 , the same as the slope in the one-parameter fit with the intercept fixed at zero. It is clear that the scatter of the data is such that the actual intercept might well be as high as, say, 1 dpm/kg SiO_2 , but not much larger. However, it is noteworthy that six of the 55 Pacific samples collected, i.e. 11% of the total, showed no measurable activity, despite having recovered silica amounts of 3–7.5 g for five of the samples [2]. Measurable activities were found in all 54 of the Atlantic and Indian ocean samples. This shows that the dissolved silica activity in Pacific deep water is indeed very close to zero. We note that the dissolved SiO_2 specific activity is very much lower than the model value (~ 9 dpm/kg SiO_2) calculated by Peng et al. [4]. We return to this question in later sections on the ^{32}Si production rate, and on the effect of silica regeneration in bottom waters.

The particulate fraction of the recovered silica is given by:

$$F_P = N_P/N_T = (A_T - A_S)/(A_P - A_S) \quad (2)$$

and one needs to know A_P to calculate F_P . As noted above, measurements of Atlantic particulates gave a mean value of 40 dpm/kg (range 20–60). We therefore use $A_P = 40$ for the Pacific particulates in order to discuss variations of the particulate fraction along the center line of the conical envelope in Fig. 1, so that with $A_S = 0$, $F_P = A_T/40$. Along this central addition vector, N_P , A_P , and A_S are constant, and the total recovered silica is given by $N_T = 65/A_T$ g. At $A_T = 40$, $N_S = 0$, $F_P = 1$, and $N_P = 1.625$ g, which is constant along this line. Then for values of A_T along the observed data range on the central axis of the cone, we have:

A_T	F_P	N_S
16	0.40	2.4
3	0.075	20.0

so that the particulate fraction varies from 7.5% to 40% over the range of the data. If we take $A_P = 60$, the range is 5% to 26.7%. These values illustrate the approximate range of the particulate fraction in Pacific GEOSECS samples.

4. Indian and Atlantic Ocean specific activities

Fig. 2 shows the specific activities of all Indian Ocean subsurface samples, plotted vs. reciprocal recovered silica. The three stations are at 0° , 20° , and 38°S , and the three highest activities are at Station 428 (38°S) at 270–2510 m depth, in the intermediate waters above the salinity maximum at 2500 m. Two of these samples were counted twice, and the errors on all three are close to statistical. These three samples with very high activities and very low amounts of recovered silica (1–2 g) appear to reflect very low recoveries of dissolved SiO_2 and yet they cluster around the median line of the lower activity data: we do not understand this. The other Indian samples lie within the ranges of the Atlantic and Pacific

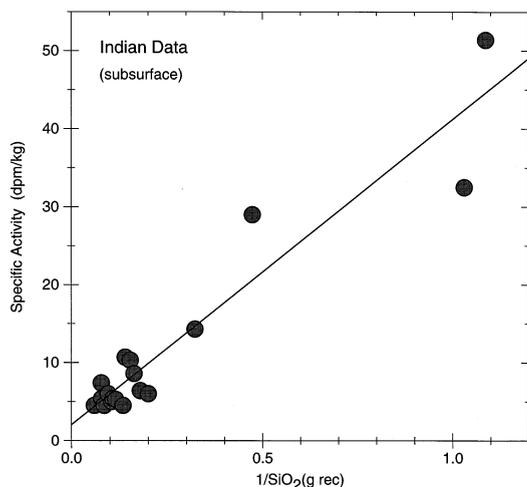


Fig. 2. ^{32}Si specific activity vs. reciprocal weights of recovered SiO_2 for all samples from the GEOSECS Indian Ocean stations. The intercept is the specific activity of dissolved silica in the Indian Ocean, $= 2.0 \pm 0.17$ dpm/kg. The mean slope is 0.039 dpm.

data for both specific activity and recovered SiO_2 . The slope of the median line is 0.039 dpm. The dissolved silica statistical specific activity given by the intercept is 2.0 ± 0.17 dpm/kg SiO_2 , and the

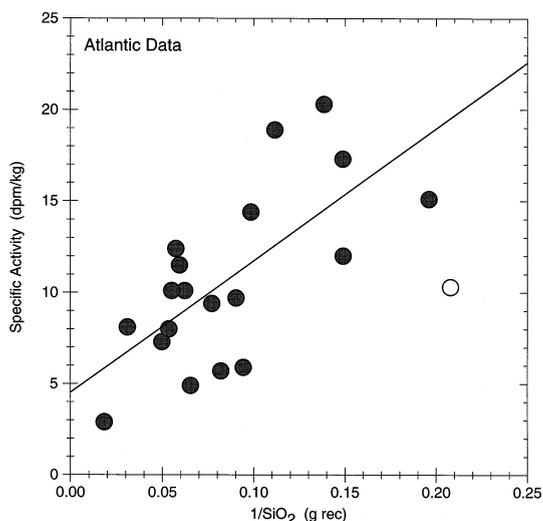


Fig. 3. ^{32}Si specific activity vs. reciprocal weights of recovered SiO_2 for all samples from GEOSECS Atlantic stations 40, 48, and 58 (27°N to 27°S). The intercept is the specific activity of dissolved silica in the Atlantic, $= 4.51 \pm 0.12$ dpm/kg. The mean slope is 0.072 dpm.

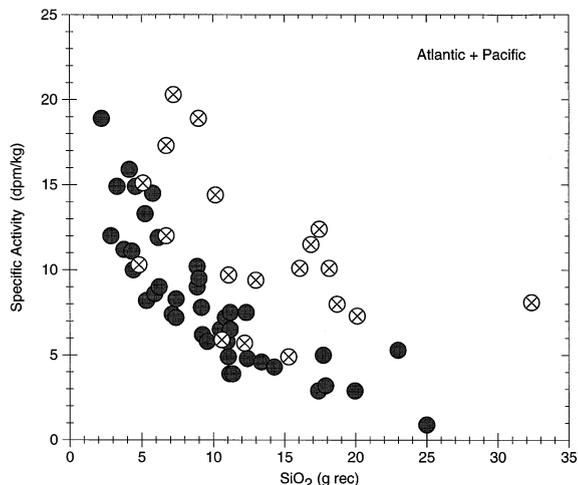


Fig. 4. Direct plots of ^{32}Si specific activities vs. recovered weights of SiO_2 , from the GEOSECS Pacific (solid circles) and Atlantic (crossed circles) samples. Note that the vertical offset of the two data sets is essentially the difference of the low activity intercepts in Figs. 1 and 3.

data form a Cornucopia plot like the Pacific samples.

Fig. 3 shows all the data from the three Atlantic stations, 27°N , 4°S , and 27°S , including the three surface water measurements all of which lie within the envelope of the deep water data. The two Antarctic stations, 45°S and 60°S , are not plotted. The solid line shows the two-parameter least-squares fit, which has a slope of 0.072, very similar to the Pacific slope (0.065), and an intercept of 4.51 ± 0.12 dpm/kg SiO_2 . The latter value is thus the nominal statistical specific activity of the Atlantic deep water dissolved SiO_2 . However, given the large scatter of the data and the relatively small number of data points, an eyeball inspection indicates to us that the actual intercept could well lie anywhere between 2.5 and 5.0 dpm/kg SiO_2 , that is, significantly lower but not much larger. The high activity biogenic silica component has a lower limit value of about 20 dpm/kg SiO_2 , only slightly higher than that for the Pacific data (16 dpm/kg), and indeed one sees that the Atlantic specific activities of recovered silica have almost entirely the same range as the Pacific data.

In Fig. 4 we plot both the Atlantic and Pacific specific activities vs. the direct weight of recovered

SiO₂, which shows the overlap of the two sets of specific activities. The Pacific data clearly approach a very low specific activity (0–1 dpm/kg) at large weights of recovered silica, and are much more tightly constrained than the Atlantic data. We note that the Atlantic samples were the first samples to be collected and analyzed and thus may have been subject to significantly larger variations in the collection and analytical techniques. Weight for weight the specific activities of the Atlantic samples are clearly offset from the Pacific values by an amount consistent with the difference in the statistical values of the low activity intercepts (~4.5 and 0 dpm/kg), which lends some confidence to the difference of the dissolved SiO₂ activities given by the intercepts. However, one sees that unfortunately the range of the Atlantic recovered SiO₂ weights does not extend far enough at either extremity to determine the degree of convergence with the Pacific curve at either high or low activities. The offset of the two curves reflects: (1) the different specific activities of dissolved SiO₂ in the two oceans, and (2) to a much lesser extent the different slopes of the median lines in Figs. 1 and 4. The two median slopes differ by only 11%, so that for the same amount of recovered particulates, the mean specific activity of Atlantic particulates is 11% greater than those of the Pacific, or conversely for the same activities, the recovered particulate phase is 11% greater than in the Pacific. The magnitude of the atmospheric input flux of ³²Si is fundamental for the understanding of these dissolved ³²Si specific activities, and we calculate this flux in Section 5.

5. The global production rate of ³²Si

In order to establish the production rate of a long-lived cosmogenic isotope, knowledge of the atmospheric fallout rate at one or more localities is required. Cosmogenic isotopes are produced primarily in the stratosphere and upper troposphere and are brought down to the lower troposphere by atmospheric circulation, where isotopes such as ³²Si are then removed by precipitation [6,7]. Because of the strong zonal atmospheric circulation, the activities are essentially uniformly

distributed along individual zonal latitude belts, so that atmospheric fallout along a given latitude is dependent only on precipitation rates, and the zonal fallout rate can be determined by measurements of mean concentrations in rainwater multiplied by the mean zonal precipitation rate at the latitude of rain collection [7]. The tropospheric component (i.e. atoms produced within the troposphere) is essentially uniform over all latitudes, since it is largely precipitated in the latitudinal zone in which it is produced. However, the stratospheric component, which is much larger, varies strongly with latitude, with a broad maximum at median latitudes reflecting the ‘dumping’ of the stratospheric burden into the troposphere in the gaps between the equatorial and polar tropopause: this behavior has been established by studies of fission products produced in nuclear explosions [8]. Thus it is necessary to know the latitudinal variation of the total zonal fallout distribution in order to calculate global production rates from individual fallout measurements, and Lal [6] and Lal and Peters [7] have presented such a curve for long-lived cosmogenic isotopes.

5.1. Previous estimates of the atmospheric input flux of ³²Si

There exists only one usable set of direct measurements of ³²Si fallout [9]: a series of rain collections at six stations in India (latitudes 10–32°N) from 1966–1970 (data prior to 1966 were influenced by thermonuclear explosions). Based on these data the global mean ³²Si flux has twice been calculated by D. Lal [1,2]. In the treatment of the GEOSECS Atlantic data [1] the zonal mean tropospheric fallout for 0–30°N was assumed to be the average of the specific activities in all the Indian rains and divided by λ (1/202 years) to give the global zonal flux $F^*(0-30^\circ)$. The mean zonal flux for latitudes 30–90° was assumed to be $1.4 \times F^*(0-30^\circ)$ as the correction for stratospheric contributions in these latitudes. Thus the mean global ³²Si flux in this calculation is $2.4 \times F^*(0-30^\circ)$ or $F^* = 2.02$ atoms/m² s.

In the treatment of the GEOSECS Pacific data [2], the global ³²Si flux was calculated differently. The tropospheric zonal mean fallout rate was cal-

culated by multiplying the mean concentration in Bombay rains by the *local* rainfall at Bombay (rather than by the zonal rainfall), and the resulting value of $F^*(0-30^\circ)$ was then multiplied by a factor of 3.11 as “the ratio of global mean production rate and the tropospheric production rate at Bombay and Khandala” (actually Bombay only, as the rainfall at Khandala is twice as high). This procedure gave a ‘mean global fallout’ of $F^* = 5.03$ atoms/m² s. The difference between these two results is a combination of a factor of 1.9 for the 0–30° zonal fluxes (due to use of the local rainfall at Bombay), and a factor of 1.3 for the assumed corrections for the stratospheric contribution. Although in each ocean the calculated global flux was very close to the mean specific activity of the recovered silica for that ocean, there can be but one ‘mean global flux’, and, in any case, the agreement is irrelevant because of the particulate component in the recovered silica. As we show in Section 5.2, these flux calculations are based on a fundamental misapprehension of the corrections for stratospheric contributions.

5.2. Calculation of the global ³²Si fallout

We return to the Indian ³²Si fallout measurements [9]. Table 1 shows the latitudes of the six stations and the ³²Si activities measured in the incremental collections, which range from periods of 2.5 to 10 months for four stations with a single increment, and cover ~4 years in 9–10 increments at Bombay and Khandala. The smoothed zonal northern hemisphere annual rainfall at the

station latitudes is taken from the values tabulated by 5° latitude zones [10]: these values multiplied by the ³²Si rainfall concentrations give the global zonal fallout values (dpm/cm² yr) at the individual latitudes, which, multiplied by (1/λ), give the zonal ³²Si fluxes (atoms/cm² s) in the final column. These are the basic data from which the global ³²Si fallout must be calculated, with regard to whether they represent tropospheric or total (stratospheric plus tropospheric) fallout values.

In the previous calculations of the ³²Si global fallout [1,2] it was assumed that the zonal fluxes represent only the tropospheric fallout component in the 0–30° latitude zone, and these fluxes were multiplied by various factors to derive the stratospheric contribution and thus the total global flux. This operation, however, was based on a misapprehension concerning the curves for tropospheric and stratospheric components presented by Lal [6] and Lal and Peters [7]. In these graphs the tropospheric (F_T), stratospheric (F_S), and total (F) fallout patterns are plotted as functions of *geomagnetic* latitude (λ). Thus the Indian rain stations (λ = 0.60–22.6°) were assumed to lie in the zone in which tropospheric fallout predominates, so that large correction factors for stratospheric production at higher latitudes had to be used to calculate the global mean fallout.

The stratospheric fallout pattern, however, is unrelated to the latitudinal variation of cosmic ray production rates in the atmosphere [6,7]. As noted above it is derived from the fission product fallout pattern from nuclear explosions [8], which is not dependent on the latitude (geographic or

Table 1
³²Si fallout in Indian rains (1966–1970)

Site	Lat °N	³² Si (dpm/10 ³ l)	Zonal rainfall (cm)	Zonal fallout (10 ⁻⁶ dpm/cm ² yr)	Zonal flux (10 ⁻⁶ atoms/cm ² s)
Pathankot (10 mos.)	32.23	0.47	71.0	33.4	112.3
Ludhiana (2.5 mos.)	30.93	0.38	69.5	26.4	88.9
Gwalior (6 mos.)	26.23	0.28	67.5	18.9	63.6
Bombay (4 yrs, <i>n</i> = 10)	18.90	0.211 ^a	80.0	16.9	56.8
Khandala (3.3 yrs, <i>n</i> = 10)	18.78	0.215 ^b	80.0	17.2	57.9
Kodaikanal (5.5 mos)	10.23	0.21	170	35.7	120

Data are for single increments collected over the time periods in column 1, except for Bombay and Khandala for which the data are the means of *n* increments collected over the total times listed. The data in column 3 are from [9], column 4 from [10].

^aMean of 9 increments, $\sigma = \pm 0.074$, $\sigma_m = \pm 0.025$ (12%).

^bMean of 10 increments, $\sigma = \pm 0.033$, $\sigma_m = 0.010$ (5%).

geomagnetic) where fission products are injected, but is determined solely by geophysics: the gaps at median latitudes where the tropopause is broken and stratospheric dumping into the troposphere takes place. Similarly, the tropospheric component, F_T , is essentially independent of geomagnetic latitude: it represents the mixing of the tropospheric component by the zonal circulation. In the fallout pattern graphs [6,7] however, plotting in geomagnetic latitude was taken over from plots of the number of nuclear disintegrations (stars) produced in an air column, which is of course a function of geomagnetic latitude with maximum production in polar latitudes. But as we note, the actual fallout patterns of cosmogenic isotopes are determined by the geographic latitudes where stratospheric dumping takes place, and by the zonal circulation.

In Table 1 we see that the ^{32}Si activities in the Indian rain collections increase progressively from south to north by a factor of 2.2 over the latitude range. The zonal rainfall values are essentially uniform ($\pm 8.5\%$) with the exception of the southernmost station, so that for the remaining five stations the global zonal fallout concentrations and fluxes increase progressively by a factor of 2 over the 13.5° range in latitude. It is noteworthy that the local annual rainfall at these stations during 1966–70 varied by a factor of 7 (70–491 cm), and that the local rainfall at Khandala was twice that of Bombay, although it is only 80 km to the southeast. The ^{32}Si concentrations and zonal fluxes, however, are independent of these large local variations.

Fig. 5 shows the cosmogenic isotope fallout patterns [6,7] plotted here in geographic latitude (ϕ) coordinates, together with the zonal fluxes of ^{32}Si derived from the Indian rain data. The zonal fluxes were fit to the normalized total fallout curve (F) by adjusting the total global flux for the best fit to the total fallout curve. One sees that, with the exception of the southernmost station, the fit of the other five stations is very good. The factor of 2 latitudinal variation in the zonal fluxes shows clearly that this is not a tropospheric fallout pattern, as the F_T tropospheric curve is very constant with latitude. The very high fallout for the southernmost station, Kodaikanal at

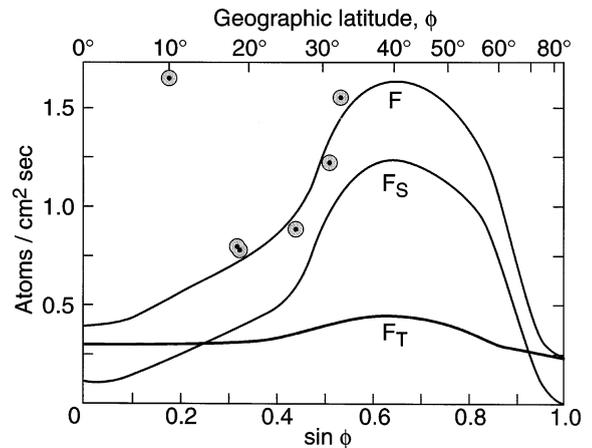


Fig. 5. Fallout pattern for long-lived cosmogenic isotopes (F_T = tropospheric, F_S = stratospheric, F = total) after Lal [6] and Lal and Peters [7], but here plotted vs. geographic latitude ϕ . The stratospheric curve is therefore that given by Machta [8]. The ordinate is scaled relative to a total global flux of 1 atom/cm² s. The points show the ^{32}Si zonal fluxes (Table 1) derived from the Indian rain concentration data [9], for the best-fit global fallout rate of 72×10^{-6} atoms/cm² s (mean deviation = $\pm 10\%$ for the five points on the curve). This is the multiplier to be applied to the scale on the ordinate.

10.23°N , is not understood. The ^{32}Si concentration in the 5.5 month 1968 increment is 0.21 dpm, similar to the rains at Bombay and Khandala 8.5° to the north, but the global rainfall at this latitude is very high (170 cm) so that the zonal fallout is about three times higher than predicted. The ^{32}Si rainfall concentration at this station was also measured in a year-long increment in 1961 [9] with a similar result (0.20), so it appears that the measured concentration is typical of this station. Kodaikanal lies in the latitude of the maximum global precipitation (2.2 m at $5\text{--}10^\circ\text{N}$), so that there may be an effect here that is not understood. Indeed the ^{90}Sr fallout data show a subsidiary maximum at 10°N which was ascribed to tropospheric fallout [8], and one wonders if there may indeed be a small stratospheric dump at this latitude.

The best fit to the total fallout curve gives $F^* = 0.72$ atoms/m² s as the global atmospheric ^{32}Si flux. This value is much smaller than the previous calculations [1,2] of 2.0 and 5.0 atoms/m² s, which assumed that the Indian rain activities rep-

resented only tropospheric production and hence required large corrections for stratospheric fallout contribution. This correction arose from plotting the fallout patterns in Fig. 5 vs. geomagnetic latitude, as is done for star production rates. (Note that the original ^{90}Sr data fallout curve was plotted vs. $\sin \phi$). When the abscissa in Fig. 5 was taken as $\sin \lambda$ (rather than $\sin \phi$) the range of observed values was shifted to $0.60\text{--}22.65^\circ$, the region in which the tropospheric component dominates the total fallout, and the mean of the individual zonal fluxes was then used as a single average tropospheric component for this range of λ . Thus large corrections for the stratospheric component in higher latitudes were required for the mean global fallout, resulting in the high values previously calculated for the total production rate.

6. Dissolved silica ocean models

Lal and Peters [11] proposed the model of the oceanic silica and ^{32}Si cycle used by Peng et al. [4]: “siliceous skeletons redissolve in the deep sea before reaching the ocean floor” and thus for ^{32}Si , “one can neglect the fraction of the isotope which is lost by deposition on the ocean floor”. Peng et al. [4] used: (1) a 1-D vertical diffusion–advection model, (2) a 10-box ‘Pandora’ box model, and (3) the Hamburg general circulation ocean model, to calculate deep ocean ^{32}Si specific activities. All three models were tuned to match the observed features of ^{14}C specific activity and dissolved silica in the oceans. The 1-D diffusion–advection model with particulate silica totally redissolved in deep water produces a broad silica maximum at ~ 1700 m because of this in situ ‘J-flux’ injected into the water column. This reproduces the silicate deep maximum in the Pacific seen from 50°N to 45°S latitudes, but in the Atlantic the silicate extremum is actually a *minimum* concentration between these latitudes, at $1500\text{--}2000$ m depth, and high silicate concentrations are found only at high southern latitudes where the northward flow of Antarctic bottom water produces a virtual silicate maximum along the bottom of the South Atlantic. The flaw in this model is simply that

these silicate extrema are predominantly horizontal advection features of the general circulation.

In a detailed study, Craig et al. [12] showed that the deep silicate maximum south of 9°S latitude in the South Pacific is an ‘induced’ advective feature created by the southward flow of North Pacific deep water above the lower silicate Antarctic bottom water, and that silica is conservative (i.e. it scales precisely with salinity and temperature) throughout this feature. Similarly, a Si–salinity plot (not shown) for GEOSECS Stn. 217 ($44^\circ40'\text{N}$) shows precisely the same features as Fig. 5 of Craig et al. [12] relative to the core water types containing the SiO_2 maximum. In the North Pacific Deep Water from 500 to 1900 m (the SiO_2 maximum) both the T–S and SiO_2 –S curves are linear, indicating that SiO_2 is conservative in this water mass. Below the advective core at 1900 m, the same curves are also linear to 4000 m (the top of the AABW mass), so that SiO_2 is seen to be conservative both above and below the horizontally advective core carrying the SiO_2 maximum. Edmond et al. [13] showed that the deep silicate maximum in the Indian Ocean is a similar ‘induced maximum’ in which high silica waters are formed by dissolution of diatomaceous sediments in northern deep waters which then are advected southward over the northward-flowing bottom water. These authors also showed that the silicate maximum in the North Pacific has a significant advective component and probably originates in the northeast Pacific by dissolution of silica from bottom sediments, where silica profiles increase to the bottom. Tsunogai [14] showed that the most extensive area of silica regeneration by dissolution from sediments into North Pacific bottom water is the Bay of Alaska, as shown by the increase of silica in bottom water profiles along 50°N to this region. Moreover, studies of the settling fluxes of biogenic silica collected in more than a dozen profiles in the world oceans [14] show that the vertical profiles of these fluxes are almost constant with increasing depth, another indication that silica in deep waters is primarily regenerated at the seafloor by dissolution of silica from sediments. Thus the fundamental premise of all three models of Peng et al., that the atmospheric input of ^{32}Si is totally recycled within the ocean itself so that the

input flux is balanced by radioactive decay within the ocean, is in conflict with the oceanographic evidence. In what follows we construct a very simple model that includes silica regeneration by solution from sediments and discuss the relationship between Atlantic and Pacific specific activities of dissolved silica in this context.

7. The ^{32}Si - SiO_2 global ocean cycle

Somayajulu et al. [1] proposed that “the greater fraction of the particulates reaches the ocean floor undissolved” and that an appreciable part of this silica then redissolves, so that “Consequently this distribution differs markedly from that of ^{14}C , whose injection occurs primarily at the surface”. Some of this regenerated silica will redissolve at the ocean–sediment interface, but some will also be injected into bottom water from pore waters rising because of sediment compaction. We use a simple model to show how the sequestering of particulate silica in siliceous sediments can affect the dissolved ^{32}Si specific activity in the different oceans. We take the mean dissolved silica concentrations in the Atlantic, Indian, and Pacific subsurface waters as 30, 105, and 130 $\mu\text{mol/kg H}_2\text{O}$ respectively (roughly estimated from the GEO-SECS Atlas sections), equivalent to 0.623, 2.55, and 3.26×10^{-3} $\text{kg SiO}_2/\text{cm}^2$, so that the Pacific/Atlantic ratio is 5.23. If the input ^{32}Si flux (0.72 atoms/ m^2 s, or 4.32×10^{-3} dpm/ cm^2) is balanced by radioactive decay in the dissolved silica in each of the world oceans, then the Atlantic, Indian, and Pacific specific activities A_S^A , A_S^I , and $A_S^P = F^*/N_S$ will be 6.93, 1.69, and 1.325 dpm/kg respectively (with the Atlantic and Pacific in the ratio 5.23). (The values in the Peng et al. models are much higher because they used the atmospheric input flux from [2].) These values are the ‘statistical activities’ and the ratio 5.23 is the ‘statistical ratio’ of deep Atlantic to Pacific dissolved silica specific activities if there is no biogenic silica. We designate this ‘statistical ratio’ as R^* . However, in our model a fraction f_S of the input is taken up by biogenic particulates which sink rapidly to the sediments and undergo radioactive decay prior to being redissolved and injected into

the bottom waters of the ocean. Thus $f_S F^*$ is the flux from the ocean to the sediments and $f_S F^* e^{-\lambda \tau}$ is the return flux to the deep waters, where τ is a mean storage time on the seafloor before this silica returns to the bottom waters. The total input of ^{32}Si into each ocean is therefore $F^*(1+f_S e^{-\lambda \tau})$. Then the deep water specific activity in each ocean is:

$$A_S = (F^*/N_S)[1-f_S(1-e^{-\lambda \tau})] \quad (3)$$

where the values of (F^*/N_S) are the ‘statistical activities’ for each ocean given above.

Because the values of A_S for the Indian and Pacific oceans are, within uncertainties, so similar to the statistical activities, no estimates of τ can be made for these oceans. However, to fix our ideas let us take the Atlantic dissolved SiO_2 value as $A_S^A = 4.5$ dpm/kg from Fig. 3. Then τ_A is 87, 117, and 167 years for $f_S = 1.0, 0.80,$ and $0.62,$ and becomes infinite at $f_S = 0.37$. These are the model mean sediment-sequestering times as a function of the fraction of the ^{32}Si atmospheric input flux to the Atlantic that is short-circuited directly to the sediments by particulate silica. The fraction of the atmospheric input that decays in the sediments prior to dissolution is equal to $f_S(1-e^{-\lambda \tau})$, i.e. it equals $1-A_S/A_S^*$ which is 35% for the Atlantic ocean.

Eq. 3 also provides insight into the difference in specific activities in deep waters of the various oceans. Again to fix our ideas, let us take $f_S \approx 1$ in both the Atlantic and Pacific. Then the ratio of deep water activities is given by:

$$R = A_S^A/A_S^P = R^* \exp[(\tau^P - \tau^A)/202] \quad (4)$$

where R^* is the ‘statistical ratio’, = 5.23 as defined above. For $\tau^P = \tau^A$, $R = R^*$, the statistical ratio. (This is also true for any values of f_S , if f_S and τ are equal for both oceans.) For $(\tau^P - \tau^A) = +110$ to -150 years, for example, the value of R varies from 9 to 3 and is thus both greater and less than R^* in this range. For $\tau^P > \tau^A$, R is greater than R^* because there is less regeneration of silica from the sediments in the Pacific. For $\tau^P < \tau^A$, R is less than R^* because the regeneration rate is greater in the Pacific. Thus

small differences in the storage times, of the order of 100 years, can change the observed ratios of A_S^A/A_S^P to significantly greater or less than the statistical ratio of the activities that would be observed if there were no biogenic particulate flux to the sediments. This emphasizes the enormous influence of the biogenic particulate flux on the distribution of specific activities in the world oceans.

Our model is of course highly simplified with respect to the actual localized distribution of the high silica sediments where silica is regenerated into the bottom waters. Also τ represents 'lumped' values of storage times for two components: the more easily dissolved diatoms and the more resistant radiolaria tests. However, the broad features are clear: the actual specific activities in deep ocean dissolved silica can be lower than required for radioactive steady state with the atmospheric input flux, because of radioactive decay in the siliceous sediments that act as a temporary storage reservoir for the biogenic particulate flux before it dissolves or is injected back into the bottom waters of the sea. It is clear that the model is primarily of heuristic interest at present: applications must await the advent of AMS techniques for ^{32}Si counting.

8. Conclusions

Silica collected on the GEOSECS sampling fibers consists of two components: (1) dissolved SiO_2 scavenged by the ferric hydroxide coating, and (2) biogenic particulate opaline silica suspended in the ambient ocean water. In a plot of specific activity vs. the reciprocal of the total recovered SiO_2 the data array consists of a conic section envelope of points, converging at the apex of the cone to A_S , the specific activity of dissolved SiO_2 , at $1/\text{SiO}_2(\text{rec})=0$. This is the resolution of the ^{32}Si Paradox. The fact that the specific activities of recovered silica lie in a similar range throughout the oceans simply reflects the gross similarity in activity of the mean biogenic particulates in the oceans, together with the much lower activities of dissolved SiO_2 , so that the ranges of the data sets are fixed by the high activity biogenic component in the mixture. The

specific activities in dissolved silica in the individual oceans are controlled by the ratio of the global ^{32}Si flux to the dissolved SiO_2 water column inventories, and modulated by the sequestering times of particulate silica in sediments prior to redissolving in the overlying bottom waters.

In deep Pacific waters the ^{14}C relationship is the result of two effects: (1) dissolution of carbonate and oxidation of organic carbon from sinking particulates adds significant amounts of CO_2 to the deep water, and (2) the particulate carbon flux (an in situ or 'J' flux) increases the ΣCO_2 concentration, but it replenishes the dissolved ^{14}C in deep water at about the same rate that it is diminished by radioactive decay [$\tau(^{14}\text{CO}_2)=\sim 8400$ years, $\tau^*(^{14}\text{C})$, the radioactive mean life, = 8266 years] so that $N^*(^{14}\text{C})$ is essentially constant [3]. But this situation is unique for radiocarbon: the measurements of dissolved ^{14}C are not affected by inclusion of trapped particulates in the collected water samples because the CO_2 concentration is so large, and there is no significant ^{14}C flux from bottom sediments into the ocean. Attempting to force the ^{32}Si data into the Procrustean bed of the oceanic ^{14}C cycle is an exercise in futility. The analysis presented here emphasizes once again that to be relevant, models must be driven by data, and not the reverse.

The GEOSECS ^{32}Si measurements are reliable and consistent (albeit in need of interpretation), and fully justify the massive investment of expedition station time (~ 12 h per profile), personnel labor in preparing 3000 kg of hydroxide-coated fibers, and analytical effort in recovering and measuring the ^{32}Si in the laboratory, on a scale not likely to be repeated ever again. The analysis and resolution of the data presented here are, as in all good models, susceptible to experimental verification, which must await the advent of AMS measurement techniques for ^{32}Si .

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