

DISTRIBUTION OF ^{32}Si IN THE WORLD OCEAN:
MODEL COMPARED TO OBSERVATION

Tsung-Hung Peng

Environmental Sciences Division, Oak Ridge National
Laboratory, Oak Ridge, Tennessee

Ernst Maier-Reimer

Max-Planck Institut für Meteorologie, Hamburg
Germany

Wallace S. Broecker

Lamont-Doherty Earth Observatory of Columbia
University, Palisades, New York

Abstract. Calculations of the $^{32}\text{Si}/\text{SiO}_2$ ratio obtained in ocean models are compared with measurements of this ratio made as part of the GEOSECS program (Somayajulu et al., 1987, 1991). A major difference is found; while the models predict threefold to fivefold higher ratios in the deep Atlantic Ocean than in the deep Pacific and Indian oceans, no such difference is seen in the measurements. This points to a flaw in the measurements. Our modeling results suggest that the most interesting application for this 120-year half-life cosmogenic isotope is as a monitor of upwelling. However, considering the expense and difficulty associated with ^{32}Si measurements, such studies may prove impractical.

INTRODUCTION

The most difficult and demanding measurements made as part of the GEOSECS survey was that of ^{32}Si , a 120-year half-life cosmogenic isotope. Sampling required the deployment of large bags stuffed with Fe-coated fibers. Measurement required ultra low level beta counting of ^{32}Si daughter isotope ^{32}P . The results of these measurements are published in two papers [Somayajulu et al., 1987, 1991]. Beyond the interpretation given by these authors, nothing is to be found in the literature regarding their significance. In this paper, the observed distribution is compared with distributions predicted from two global ocean models. The first of these is a

10-box reservoir model whose biological and physical transfer coefficients have, by iteration, been set to achieve a match to the major features of the distributions of $^{14}\text{C}/\text{C}$ and dissolved silicate in the sea [Broecker and Peng, 1986, 1987]. The other is an ocean general circulation model (GCM) tuned to fit the distributions of these same properties [Maier-Reimer and Bacastow, 1990].

Silicon 32 is produced in the atmosphere by cosmic rays. The newly born "hot" atoms become attached to aerosols and are removed to the earth's surface in precipitation. Roughly 70 percent of these atoms are added directly to the sea. Some, but not all, of the remaining 30 percent reach the sea via rivers. The remainder undergo radiodecay during transit to the sea. Those ^{32}Si atoms which enter the sea mix with the stable silica and join the marine silicate cycle. The addition of ^{32}Si to the sea surface is not geographically uniform (more reaches the rainfall at high than at low latitudes). Within any given latitude belt ^{32}Si fallout should correlate with rainfall. At any given site its input will be stochastic coming with rain events.

The dissolved silicate added to the sea from rivers resides about 40,000 years before being removed to the sediments [Broecker and Peng, 1982]. While in the sea, this silicate is intensely cycled between dissolved and opaline form. Diatoms and radiolarians manufacture opal in the upper ocean. This opal falls through the water column and eventually redissolves. In combination with the sea's thermohaline circulation this cycle generates extremely large chemical gradients; the silica concentration ranges over three orders of magnitude. Warm surface waters are nearly free of silicate ($<1 \mu\text{mol kg}^{-1}$). Deep waters show a progression in silicate content from about $10 \mu\text{mol kg}^{-1}$ for new North Atlantic Deep Water (NADW) to $40 \mu\text{mol kg}^{-1}$ for

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TABLE 1. Summary of ^{32}Si Measurements on Surface Water

GEOSECS Station	Latitude	Longitude	SiO_2 , $\mu\text{mol/kg}$	$^{32}\text{Si}/\text{SiO}_2$, dpm/kg^\dagger
<i>Atlantic Ocean Surface Water</i>				
401*	27°N	54°W	1.0	10.1
48	4°S	29°W	1.3	15.1
58	27°S	37°W	0.6	20.3
67	49°S	51°W	0.4	47.9
<i>Pacific Ocean Surface Water</i>				
202	33°N	140°W	2.4	81.5
337	5°N	124°W	7.3	9.4
263	17°S	167°W	2.1	8.4
306	33°S	164°W	6.4	64.5
<i>Indian Ocean Surface Water</i>				
420	0°	51°E	2.8	6.4
452	20°S	80°E	2.1	14.8
428	38°S	58°S	0.7	29.6
<i>Antarctic Ocean Surface Water</i>				
89	60°S	0°	55.5	9.8
282	58°S	170°E	3.4	27.9

Data are from: Somayajulu et al. [1987, 1991].

*IndoMed Expedition November 1977.

$^\dagger 1 \text{ dpm/kg} = 9.08 \times 10^{-18} \text{ atoms } ^{32}\text{Si} / \text{atoms } ^{28}\text{Si}$.

ambient NADW to $125 \mu\text{mol kg}^{-1}$ for circum-Antarctic deep water to $140 \mu\text{mol kg}^{-1}$ for deep water in the equatorial Indian and Pacific oceans and, finally, to $225 \mu\text{mol kg}^{-1}$ in the deep Bering Sea. Because silicate is recycled within the sea 40 or so times before removal to

TABLE 2. Silicon 32 Results on Particulates Collected From Surface Atlantic Ocean as Part of the GEOSECS Program

Sample	Latitude Range	$^{32}\text{Si}/\text{SiO}_2$, dpm/kg^\dagger
AP-1	64°N-50°N	60 ± 17
AP-4	36°N-2°S	50 ± 12
AP-2	30°S-55°S	35 ± 5
AP-3	50°S-61°S	20 ± 3

Data are from Somayajulu et al. [1987].

$^\dagger 1 \text{ dpm/kg} = 9.08 \times 10^{-18} \text{ atoms } ^{32}\text{Si} / \text{atoms } ^{28}\text{Si}$.

the sediment, its distribution within the sea is not influenced by the geometry of the addition to or removal from the sea. Rather it depends entirely on the interaction between biological cycling and the sea's thermohaline circulation.

OBSERVATIONS

We focus our analysis on the contrast among three water types: Atlantic deep water, Pacific and Indian deep water, and surface water. The results of measurements made by Somayajulu et al. [1987, 1991] on samples from these water masses are summarized in Tables 1 to 4 and in Figure 1. Perhaps the biggest surprise is the near uniformity of the $^{32}\text{Si}/\text{SiO}_2$ ratios. Despite the small ratio of the ^{32}Si half-life (~120 years) to ocean mixing time (~1000 years), ^{32}Si is distributed much as it would be were its half life comparable to the time for ocean mixing. The explanation for the rapidity with which ^{32}Si is spread through the ocean lies in the opal cycle. Within a year or so after entry into the sea ^{32}Si atoms are

TABLE 3. Summary of ^{32}Si Results on North Atlantic Deep Water and Antarctic Bottom Water

GEOSECS Station	Latitude	Longitude	Depth, m	SiO_2 , $\mu\text{mol/kg}$	$^{32}\text{Si}/\text{SiO}_2$, dpm/kg
<i>North Atlantic Deep Water</i>					
401*	27°N	54°W	2140	24	2.9
			3050	33	8.1
			3979	44	12.4
			4484	48	18.9
48	4°S	29°W	1779	19	10.3
			2780	32	4.9
			3678	34	5.9
58	27°S	37°W	1773	29	9.4
			2691	31	8.0
			3367	42	12.0
<i>Antarctic Bottom Water</i>					
58	27°S	37°W	4464	125	5.7
67	45°S	51°W	5385	128	22.8
89	60°S	0°	4000	119	21.7
			4805	112	18.2

† Indomed Expedition November 1977.

TABLE 4. ^{32}Si Results on Deep Waters in the Pacific and Indian Oceans

GEOSECS Station	Latitude	Longitude	Depth, m	SiO_2 , $\mu\text{mol/kg}$	$^{32}\text{Si}/\text{SiO}_2$, dpm/kg
<i>Pacific Ocean</i>					
217	45°N	177°W	1285	160	7.5
			2485	173	9.5
			3585	162	8.6
			5185	166	5.0
202	33°N	140°W	1534	154	9.0
			4592	155	17.5
227	25°N	170°E	1198	134	7.8
			2996	154	9.0
			4246	145	6.2
239	6°N	172°W	1502	125	2.9
			2608	156	3.2
			3713	147	3.9
			5422	130	8.2
337	5°N	124°W	1448	128	0.9
			1951	145	6.5
			2657	155	7.4
			3362	152	18.9
			4370	138	4.3
263	17°S	167°W	1178	85	4.6
			1981	119	11.2
			2984	132	4.8
			4488	121	5.8
			5390	122	5.3
317	24°S	127°W	1986	115	10.0
			2989	124	3.9
			3340	124	15.9
306	33°S	164°W	1660	90	11.9
			3189	128	13.3
			4051	113	22.7
			4868	122	14.9
282	58°S	170°E	1759	90	2.9
			2237	98	14.9
			3358	117	6.5
<i>Indian Ocean</i>					
420	0°	51°E	1633	109	5.4
			2549	130	5.3
			3567	134	5.4
			4585	130	6.0
452	20°S	80°E	1140	85	5.0
			1890	110	10.3
			2490	126	6.4
			3610	130	4.5
428	38°S	58°E	1820	72	14.3
			2510	83	29.0
			3560	110	4.5
			5120	135	7.4

Data are from Somayajulu et al. [1991].

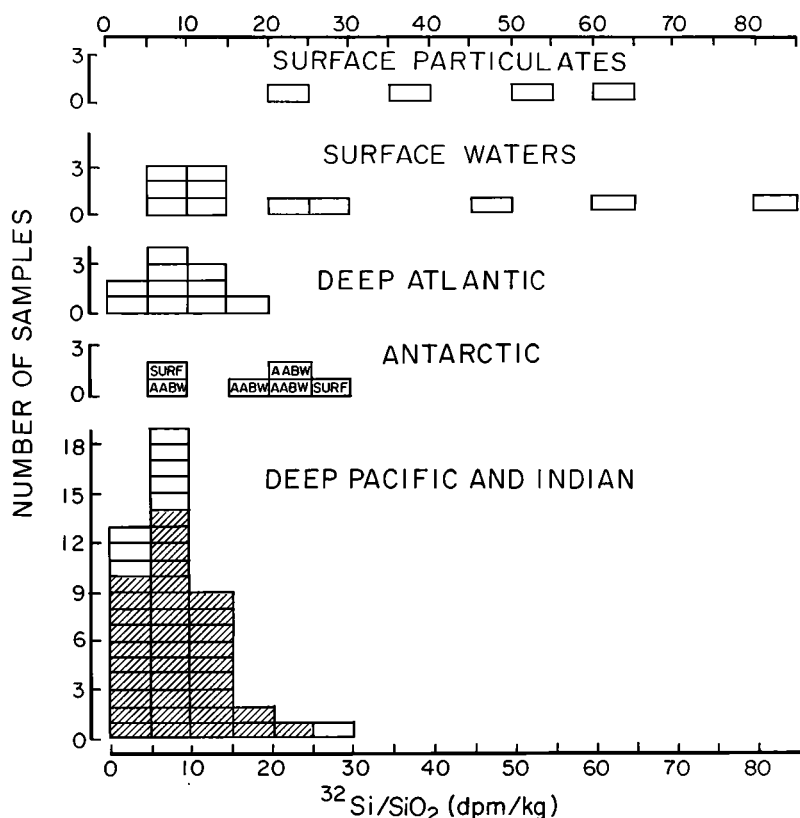


Fig. 1. Histogram summarizing the $^{32}\text{Si}/\text{SiO}_2$ results obtained by Somayajulu et al. [1987, 1991]. In the lower histogram the filled rectangles are for Pacific samples and the open ones for Indian samples. The particulate samples were collected through a bow pump while the ship was underway.

incorporated into opal. This opal falls toward the seafloor and promptly dissolves. Thus on a very short time scale, the ^{32}Si atoms are spread throughout the body of the sea.

While the opal cycle rapidly spreads the ^{32}Si with depth, lateral transport via thermohaline circulation takes much longer. Consequently, the vast majority of the ^{32}Si atoms do not survive long enough to escape the ocean to which they were added. Difficult to understand in this regard is the absence of a difference in the $^{32}\text{Si}/\text{Si}$ ratio between deep Atlantic and deep Pacific water. Per unit volume, the two oceans receive similar amounts of ^{32}Si through atmospheric fallout. As deep Pacific water has on the average five times more silica than deep Atlantic water (see Figure 2) one would expect that it would have a correspondingly lower $^{32}\text{Si}/\text{Si}$ ratio. Rather, as seen in Figure 1, the average $^{32}\text{Si}/\text{Si}$ ratio for the measurements in these two deep water masses are nearly identical. No discernible pattern exists with either water depth or with latitude, as shown in Tables 3 and 4.

One-Dimensional Model

Before considering the results of distributions obtained in the global models, it is instructive to consider

a simple one-dimensional case where water upwells through a 3800-m-high column. We adopt an upwelling rate of 5 m yr^{-1} and a uniform vertical eddy diffusivity of $1.3 \text{ cm}^2 \text{ s}^{-1}$. The water reaching the top of the column is pumped back to the bottom as new deep water. The mean column SiO_2 concentration is set at $120 \mu\text{mol kg}^{-1}$. In the surface mixed layer (75 m thick) dissolved silica is transformed to opal. The residence time with regard to biological uptake is varied so as to achieve a range of surface water silicate concentrations. Once formed, opal is instantaneously spread down the water column and redissolved. The characteristic sinking depth is 2 km. Silicon 32 is added to the surface of the column at the rate of $4.26 \text{ atoms m}^{-2}\text{s}^{-1}$. This input value is based on the measured inventory of ^{32}Si in the ocean [Somayajulu et al., 1987, 1991].

Plots of the depth distribution of dissolved SiO_2 and of the $^{32}\text{Si}/\text{SiO}_2$ ratio are shown in Figure 3 for three residence times with regard to biological removal; 1, 0.1 and 0.025 years. The corresponding steady-state SiO_2 concentrations in the surface mixed layer are 13.5, 1.5 and $0.38 \mu\text{mol kg}^{-1}$. Despite the large range in residence time, the mixed layer $^{32}\text{Si}/\text{SiO}_2$ ratio remains nearly unchanged. The reason is that the rate of SiO_2 delivery to the surface mixed layer remains nearly unchanged. Hence

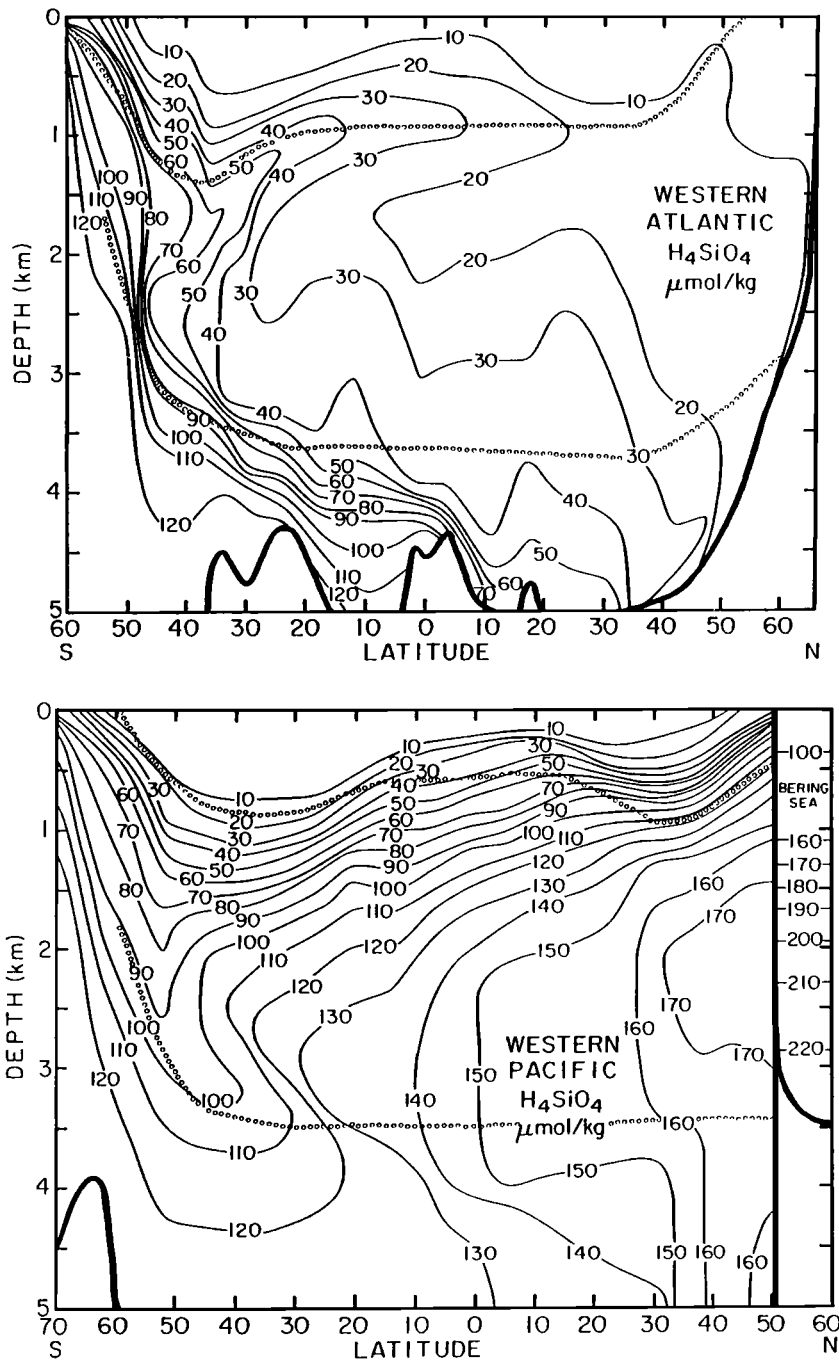


Fig. 2. Sections of silicate through the western Atlantic and western Pacific oceans (based on measurements made during the GEOSECS program).

the ratio of ^{32}Si added from above to the amount of SiO_2 added from below is close to constant.

Note that the $^{32}\text{Si}/\text{SiO}_2$ ratio for surface water is only 3 times higher than that for deep water despite the 760 year (i.e., $3800 \text{ m}/5 \text{ m yr}^{-1}$) flushing time of the column. As already mentioned, the reason is that

^{32}Si atoms newly delivered are rapidly spread through the water column through the dissolution of diatoms.

The factor controlling the $^{32}\text{Si}/\text{SiO}_2$ ratio in surface water is the water replacement time at the surface. In order to demonstrate this we halved ($W = 2.5 \text{ m yr}^{-1}$ and $K = 0.65 \text{ cm}^2 \text{ s}^{-1}$) and doubled ($W = 10 \text{ m yr}^{-1}$ and

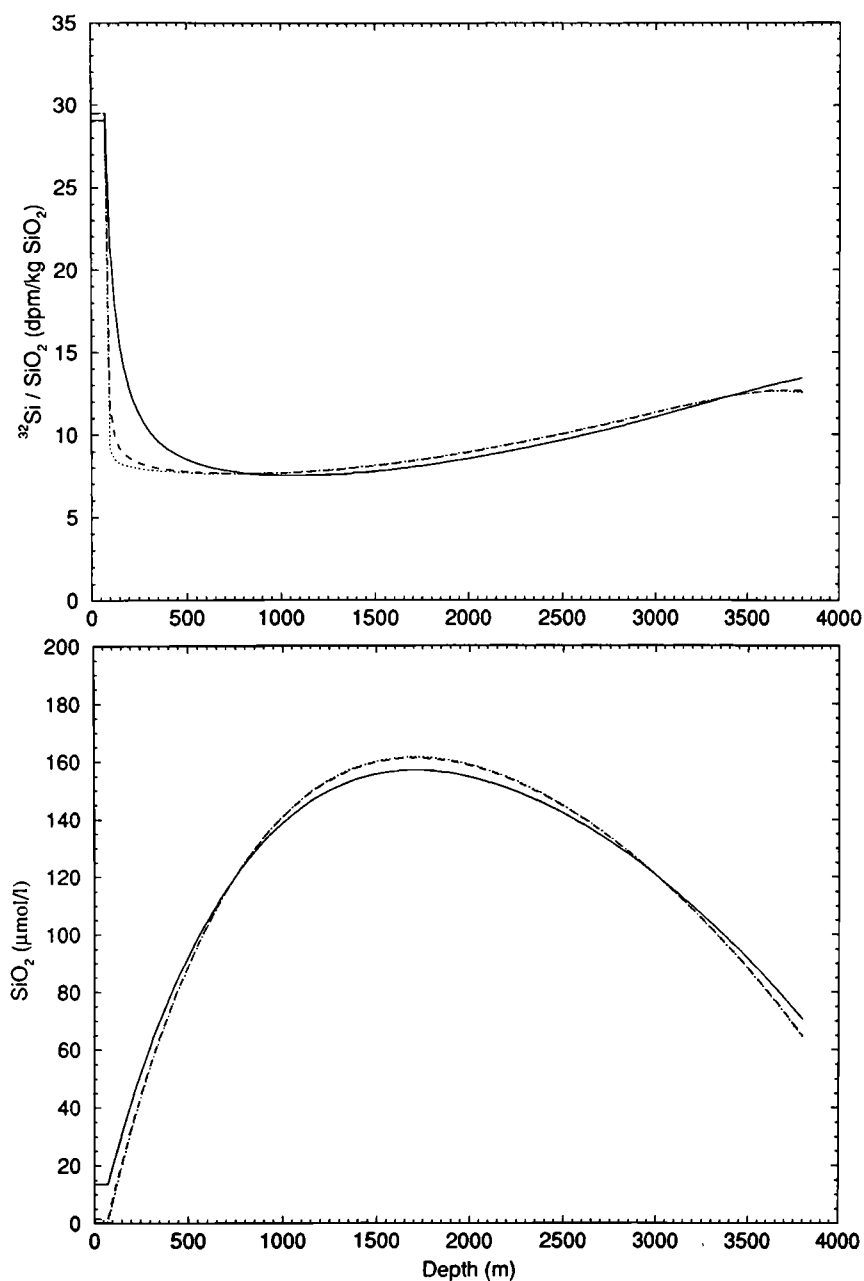


Fig. 3. Silicate concentration and $^{32}\text{Si}/\text{SiO}_2$ ratio versus depth in one-dimensional column ($W = 5 \text{ m yr}^{-1}$, $D = 1.3 \text{ cm}^2 \text{ s}^{-1}$) for three different residence times with respect to biological removal (dotted for $\tau = 0.025 \text{ yr}$, dashed for $\tau = 0.01 \text{ yr}$, and solid for $\tau = 1 \text{ yr}$).

$K = 2.6 \text{ cm}^2 \text{ s}^{-1}$) the advection velocity and eddy mixing coefficients holding the residence time for biological removal of silica from the surface mixed layer constant (at 1 year). This created a range of $^{32}\text{Si}/\text{SiO}_2$ ratios extending from 19 dpm kg^{-1} for the fast rate to 50 dpm kg^{-1} for the slow rate (see Figure 4).

Ten-Box Model

The PANDORA multibox model of Broecker and Peng [1986, 1987] is used to explore the difference in $^{32}\text{Si}/\text{SiO}_2$ expected between deep waters in the Atlantic Ocean and those in the Pacific and Indian Oceans. The

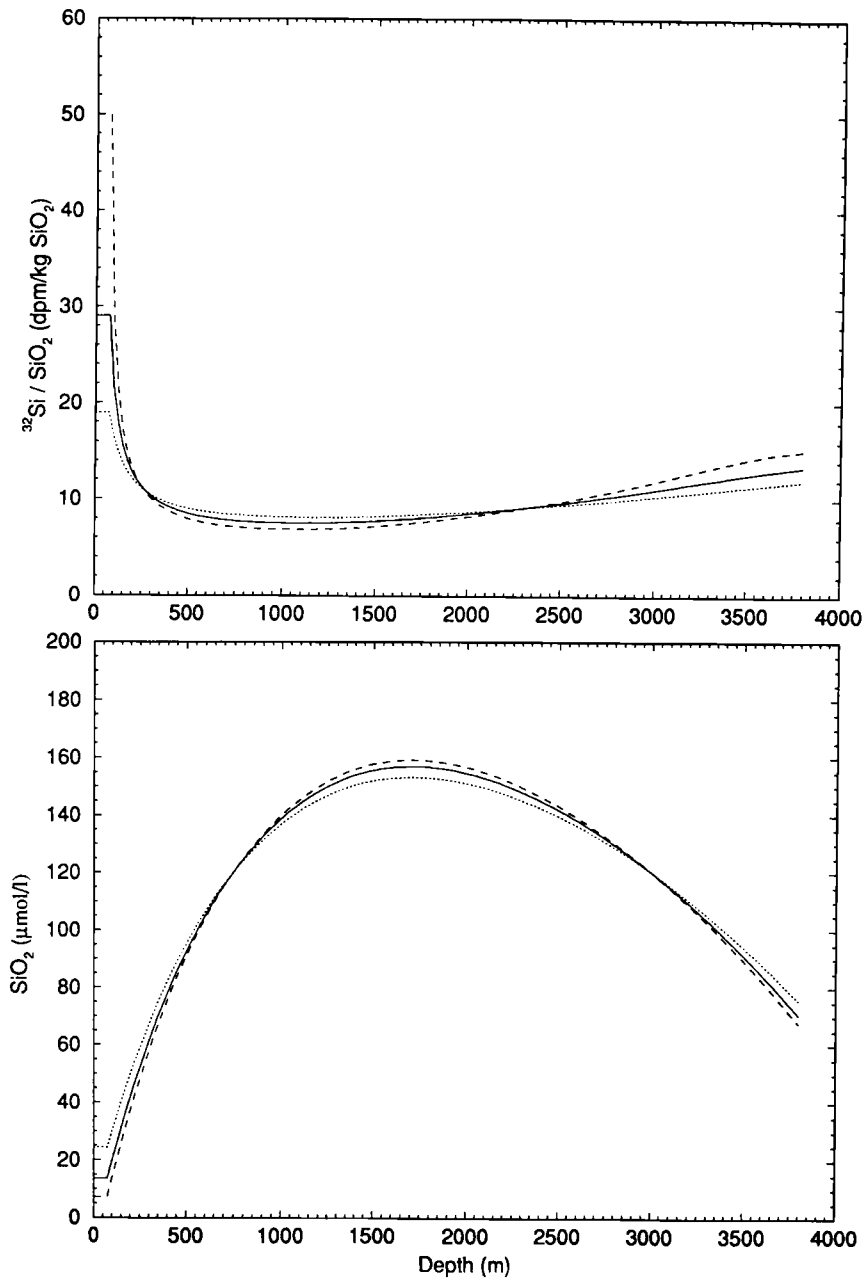


Fig. 4. The $^{32}\text{Si}/\text{SiO}_2$ and silica concentration versus depth in the one-dimensional column for three different sets of dynamics ($W = 10 \text{ m yr}^{-1}$, $D = 2.6 \text{ cm}^2 \text{ s}^{-1}$ dotted curves; $W = 5 \text{ m yr}^{-1}$, $D = 1.3 \text{ cm}^2 \text{ s}^{-1}$ solid curve and $W = 2.5 \text{ m yr}^{-1}$, $D = 0.65 \text{ cm}^2 \text{ s}^{-1}$ dashed curve) in all three cases the residence time for biological uptake (as opal) is held the same ($\tau = 1 \text{ yr}$).

architecture of this model is shown in Figure 5. The water fluxes are fixed to reproduce the first-order features of the global radiocarbon distribution. Residence times with respect to extraction of SiO_2 from the surface boxes into opal and the fate of this opal (i.e., where it dissolves) are chosen so as to reproduce the first-order

features of the oceanic silica distribution. ^{32}Si atoms are added in a geographically uniform manner to the model's surface boxes at the rate of $4.26 \text{ atoms m}^{-2} \text{ s}^{-1}$. As can be seen in Figure 5 (see also Table 5), the model generates a very different $^{32}\text{Si}/\text{SiO}_2$ ratio in the deep Atlantic reservoir than in the deep Pacific and Indian reservoir.

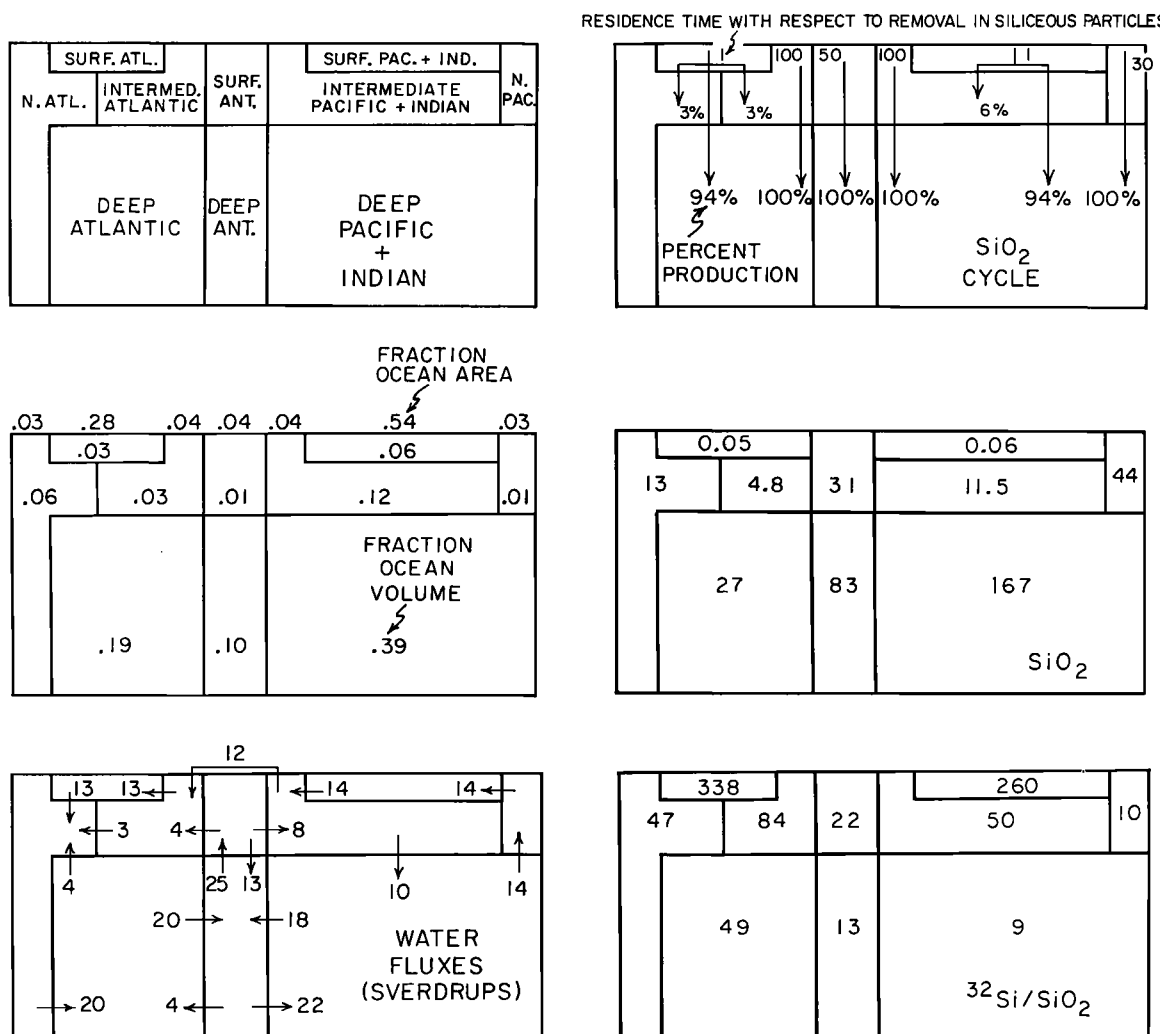


Fig. 5. The architecture of the PANDORA multibox model, its silica cycle, its silica distribution and its ³²Si/SiO₂ distribution.

As one would intuitively expect the concentration of ³²Si atoms is more nearly the same in these two reservoirs, (i.e., 26.6 CO₂ μmol kg⁻¹H₂O x 49 dpm kg⁻¹ SiO₂ or 1300 for the deep Atlantic reservoir and 167 μmol kg⁻¹H₂O x 9 dpm kg⁻¹SiO₂ or 1500 for the deep Pacific and Indian reservoir). During the 175 year mean lifetime of ³²Si atoms, relatively little silica is exchanged between these reservoirs.

Hamburg Ocean GCM

The Hamburg ocean general circulation model [Maier-Reimer and Hasselmann, 1987; Maier-Reimer and Bacastow, 1990; Bacastow and Maier-Reimer, 1990, 1991] has been programmed to reproduce the main features of the distribution of silicate in the world ocean. This was accomplished by tuning opal production rates and opal

dissolution depths so as to obtain a match to observation. The resulting silica distribution (see Figure 6) compares reasonably well with observation (see Figure 2).

Silicon 32 was added at a geographically uniform rate (4.26 atoms m⁻² s⁻¹) to the surface of the model. The

TABLE 5. Distribution of Silicate and of ³²Si/SiO₂ Ratios in Six of PANDORA's 10 Boxes

Reservoir	SiO ₂ , μmol/kg	³² Si/SiO ₂ , dpm/kg
Surface Atlantic	0.05	338
Deep Atlantic	27	47
Surface Antarctic	31	22
Deep Antarctic	82	13
Surface Pacific and Indian	0.06	260
Deep Pacific and Indian	167	9

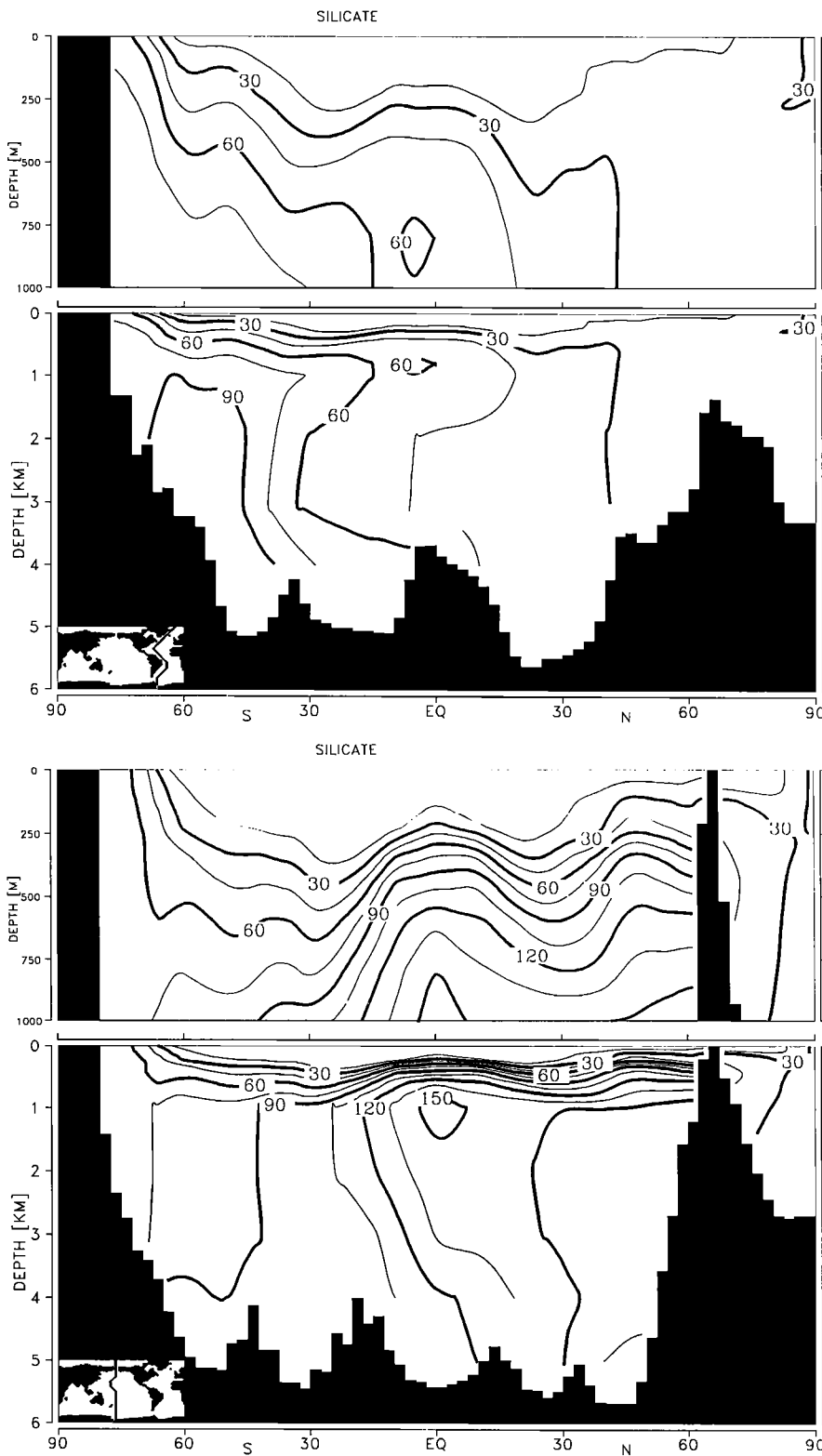


Fig. 6. Distribution of silicate ($\mu\text{mol kg}^{-1}$) in the western Atlantic and western Pacific oceans as obtained in the Hamburg general circulation model.

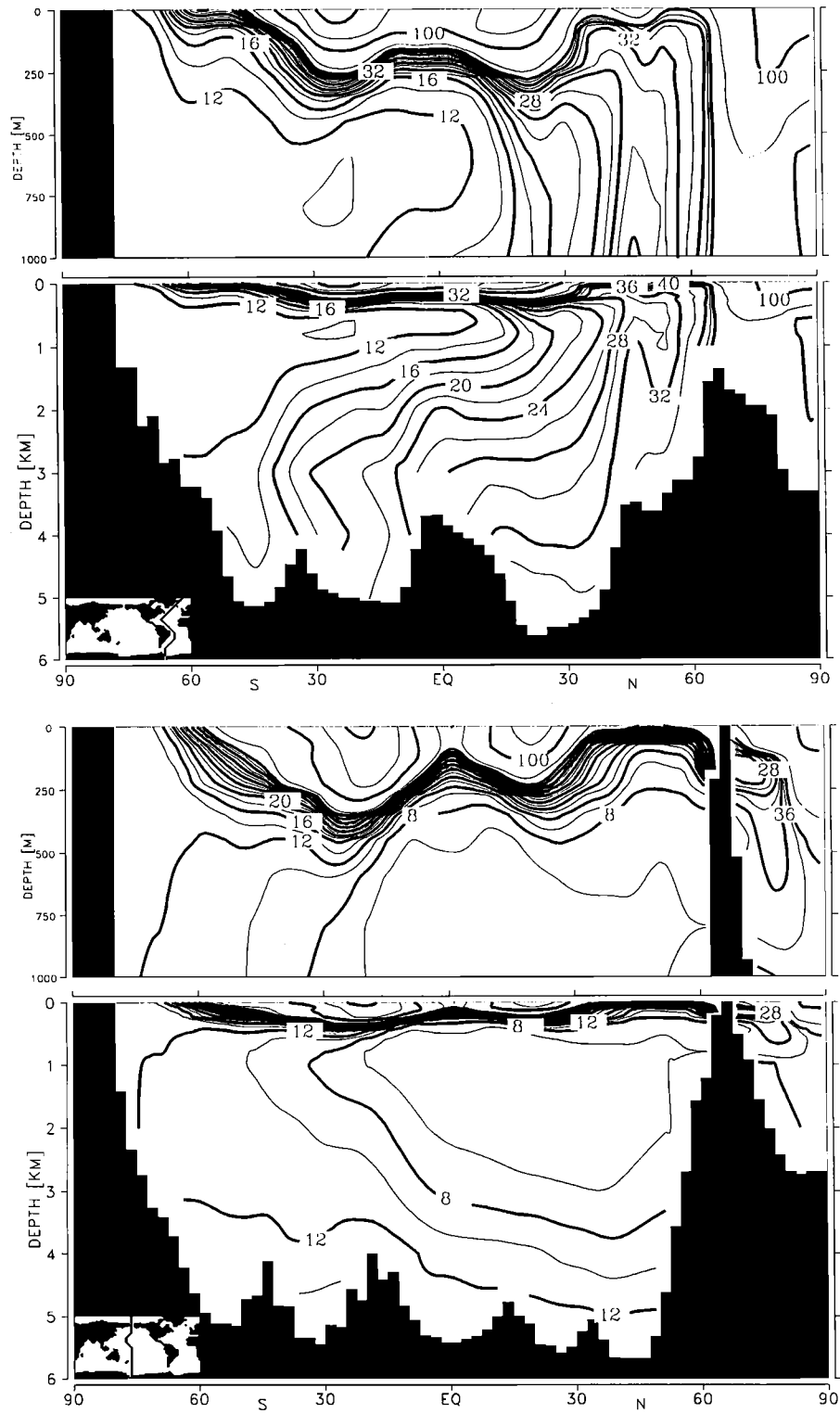


Fig. 7. Distribution of $^{32}\text{Si}/\text{SiO}_2$ ratios (dpm kg $^{-1}$) in the western Atlantic and western Pacific oceans.

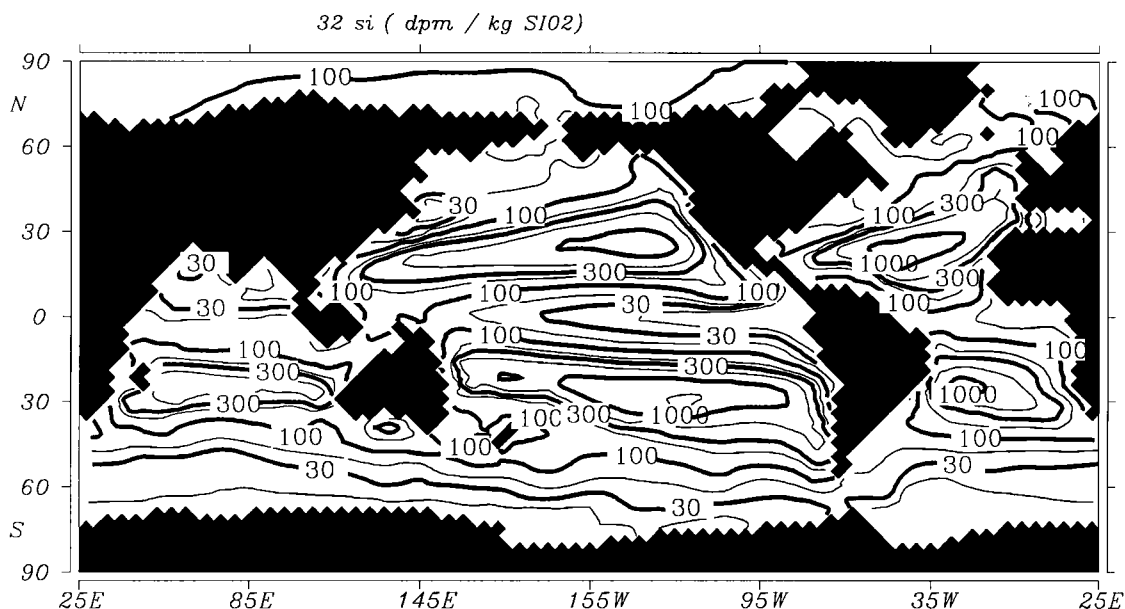


Fig. 8. Distribution of Si/SiO_2 ratios (dpm kg^{-1}) in surface waters obtained from Hamburg general circulation model.

resulting distribution of ^{32}Si to SiO_2 ratios is shown in Figure 7. As can be seen the ratio in the deep Atlantic averages about 24 dpm $\text{kg}^{-1}\text{SiO}_2$ while that in the deep Pacific averages about 8 dpm $\text{kg}^{-1}\text{SiO}_2$. As there is a threefold difference in the silica content of these two reservoirs, the concentration of ^{32}Si atoms is, as expected, nearly the same.

In Figure 8 is shown the distribution of $^{32}\text{Si}/\text{SiO}_2$ ratios in the model's surface waters. They reflect the water replacement rate. Where the replacement is rapid (i.e., in the equatorial Pacific, Arabian Sea and at high latitudes) the $^{32}\text{Si}/\text{SiO}_2$ ratios are low and where the replacement rate is slow (i.e., in the temperate gyres) the ratios are high. It must be pointed out that were the geographic dependence of the input of ^{32}Si to the ocean included in the model, details of this pattern would change, but the basic structure would remain the same. Also, at any given point on the ocean surface there would be temporal changes in the ratio associated with rainfall events.

DISCUSSION

We have no satisfactory explanation for the fundamental difference between the observed distribution of $^{32}\text{Si}/\text{SiO}_2$ ratios in the deep ocean and that obtained in the models. Perhaps the entire data set is flawed. One other distant possibility is that while nearly all the opal which forms elsewhere in the world ocean dissolves, that formed in the Atlantic is largely removed to the sediment. In other words, 70 to 80% of the ^{32}Si arriving at the sea surface would be short circuited to the sediment and never appear in the deep water. But this does not make chemical sense.

In our estimation, the resolution of this dilemma will require the collection of new samples from the deep Pacific and Atlantic. The advent of accelerator mass spectrometry (AMS) provides a new option for measurement. However, since the $^{32}\text{Si}/^{28}\text{Si}$ atom ratios for oceanic Si (10^{-15} to 10^{-16}) lie well below the current detection limit for AMS, this approach will require major improvements in AMS technique. In particular a way will have to be found greatly reduce the ^{32}Si beam without cutting down the ionization efficiency. At the time this paper was written the ETH group at Zürich was experimenting with a gas-filled magnet (M. Suter, personal communication, 1991) for this purpose.

CONCLUSIONS

Because of its half-life (120 years) and chemistry, ^{32}Si is a seductive isotope for application to studies of the marine silica cycle. However, existing measurements show little surface to bottom or ocean to ocean variation. While models suggest that larger variations should be found, harnessing them for biogeochemical use will prove extremely difficult both because the measurements are so difficult and because of the stochastic nature of the ^{32}Si input. We fear that the lure of ^{32}Si will remain more a dream than a reality.

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REFERENCES

- Bacastow, R., and E. Maier-Reimer, Ocean-circulation model of the carbon cycle, *Clim. Dyn.*, 4, 95-125, 1990.
- Bacastow, R., and E. Maier-Reimer, Dissolved organic carbon in modeling oceanic new production, *Global Biogeochem. Cycles*, 5, (1), 71-85, 1992.
- Broecker, W. S., and T.-H. Peng, *Tracers in the sea*, 690 pp., Eldigio, Palisades, New York, 1982.
- Broecker, W.S., and T.-H. Peng, Carbon cycle: 1985, Glacial to interglacial changes in the operation of the global carbon cycle, *Radiocarbon*, 28, (2A), 309-327, 1986.
- Broecker, W. S., and T.-H. Peng, The role of CaCO_3 compensation in the glacial to interglacial atmospheric CO_2 change, *Global Biogeochem. Cycles*, 1, 15-39, 1987.
- Maier-Reimer, E., and K. Hasselmann, Transport and storage of CO_2 in the ocean- An inorganic ocean-circulation carbon cycle model, *Clim. Dyn.*, 2, 63-90, 1987.
- Maier-Reimer, E., and R. Bacastow, Modeling of geochemical tracers in the ocean, *Clim. Ocean Interaction*, edited by M. E. Schlesinger, 233-267, 1990.
- Somayajulu, B. L. K., R. Rengarajan, D. Lal, R. F. Weiss, and H. Craig, GEOSECS Atlantic ^{32}Si profiles, *Earth Planet. Sci. Lett.*, 85, 329-342, 1987.
- Somayajulu, B. L. K., R. Rengarajan, D. Lal, and H. Craig, GEOSECS Pacific and Indian Ocean ^{32}Si profiles, *Earth Planet. Sci. Lett.*, 107, 197-216, 1991.

W. S. Broecker, Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964.

E. Maier-Reimer, Max-Planck Institut für Meteorologie, Hamburg 13, Germany.

T.-H. Peng, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37830-6335.

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