^{32}SI DATING OF MARINE SEDIMENTS FROM BANGLADESH

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ABSTRACT. Appropriate dating tools are essential for paleoenvironmental studies. Cosmogenic ^{32}Si with a half-life of about 140 years is ideally suited to cover the dating range 30–1000 years. Here we have applied scintillation spectrometry for detection of natural ^{32}Si to date marine shelf sediments. High detection efficiency, combined with stable background, allows for the detection of extremely low ^{32}Si specific activities found in such sediments with counting rates below one count per hour. For a sediment core from the Ganges-Brahmaputra delta ^{32}Si dating yields mean sedimentation rates of 0.7 ± 0.2 cm/yr for 50 to several hundred years BP and 3.1 ± 0.8 cm/yr for the past 50 years. The four-fold increase of the sedimentation rate over the past 50 years may reflect increased sediment loads in the rivers due to increasing human colonization within the rivers' drainage basins.

INTRODUCTION

Sediments are useful natural archives containing a wealth of environmental information and providing a high-resolution chronology of paleoenvironmental proxies. However, even annually laminated sequences with high-resolution chronologies obtainable by varve-counting require absolute dating. Such sequences are often incomplete, have variable numbers of layers produced in any one particular year, or are disturbed by erosion or deposition of dislocated material. If complete annual layering cannot be convincingly demonstrated by other means, confirmation of the relative chronology by absolute dating is necessary. Sediments without annual layers rely entirely on absolute dates.

Useful tools for determining absolute ages of sediments deposited within the last 100 years include ^{210}Pb (half-life = 22 years), ^{137}Cs (half-life = 30 years), and bomb radiocarbon. Cosmogenic ^{14}C, with a half-life of 5730 years can date only samples older than 350–1000 years, taking into account the uncertainty of the reservoir effect. Cosmogenic ^{32}Si, with a half-life of about 140 years, can be applied in the age range 30–1000 years and is ideally suited to fill the time gap. An appropriate dating tool for that time range is essential because it includes three very important epochs: the impact of human colonization and industrialization during the last 150 years, the Little Ice age between about 1650 AD and 1850 AD, and the last part of the Medieval Climatic Optimum. Hence, through the provision of absolute chronologies in sediments over the last millennium with high time and spatial resolution ^{32}Si dating has the potential to help identify human impacts on local and global environmental processes.

^{32}Si, produced in the atmosphere through cosmic ray interactions, is transported rapidly to the earth's surface mainly by rain and snow. Since its discovery by Lal et al. (1960), the potential of ^{32}Si to help understand environmental processes such as glacier dynamics, ocean and atmospheric circulation, sedimentation in lakes and oceans, and groundwater flow has been investigated by several researchers and research groups (e.g. Dansgaard et al. 1966; Nijampurkar et al. 1966; Kharkar et al. 1969; Lal et al. 1970, 1976; Krishnaswami et al. 1971; Clausen 1973; DeMaster and Cochran 1982; Fröhlich et. al. 1987; Somayajulu et al. 1991; Nijampurkar and Rao 1992; Martin et al. 1992; Morgenstern et. al. 1995, 1996, 2000; Craig et al. 2000).

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Detection of ^{32}Si is, however, very difficult due to its extremely low natural specific activity and the vast excess of stable silicon (i.e. low ^{32}Si/Si ratio). Difficulty in setting up home-built ultra low background systems has hampered wider use of ^{32}Si dating. We have applied scintillation spectrometry for detection of natural ^{32}Si using a Quantulus™ that offers high detection sensitivity and background stability and the advantages of automated measurement and data processing.

PRINCIPLES OF ^{32}SI DATING

Within the surface waters of lakes and oceans ^{32}Si builds up in the skeletons of siliceous organisms, predominantly diatoms and radiolarians. After these organisms die they settle into deep water where part of the biogenic silica dissolves. However, portions of the skeletons escape dissolution and become buried in the sediment. There, biogenic silica is a stable component suitable for dating within the time range of 10^3 years; dissolution occurs only over time scales of 10^6 to 10^9 years (Treguer et al. 1995).

^{32}Si ages are obtained from a large amount of sediment (>100 g). Although this does not allow for high age resolution for a given core diameter, the accumulation of ^{32}Si in the whole sediment sample buffers the ^{32}Si age against any small-scale variability in sedimentation rate. The ^{32}Si age signal is acquired continuously over the entire time of sediment accumulation with the biogenic silica from the overlaying water column assumed to have relatively constant atmospheric ^{32}Si input. ^{32}Si ages are not obtained from single sediment particles of questionable origin or from single variable events. The transfer of the ^{32}Si signal into the sediment depends only on gravimetric settling of biogenic silica into the sediment and is unaffected by geochemical conditions or grain-size effects. Many sediments contain biogenic silica as a main component.

Silica biomass production in many hydrologic systems is strongly seasonal, but this is assumed to have little affect on ^{32}Si dating. Little seasonal variation in ^{32}Si deposition has been observed and most seasonality in ^{32}Si and Si input will be smoothed out in the hydrologic system prior to the silica uptake by the siliceous organisms. Good agreement was found for ^{32}Si/Si in water and surface sediments (Nijampurkar et al. 1998).

The ^{32}Si specific activity of recent biogenic silica in the ocean is only about 10 dpm/kg SiO_2 (Lal 1976; DeMaster 1980) and about 15 dpm/kg SiO_2 in the Antarctic ocean (Kharkar et al. 1969), whereas in lakes it is 5–80 dpm/kg SiO_2 (Martin et al.1992; Nijampurkar et al. 1998). Such low specific activities result in count rates of about one count per hour for 0.1–1.0 kg samples. To use biogenic silica for dating over the time range 30–1000 years, even smaller count rates must be detected, and extremely low background systems with very stable detection parameters are necessary. Additionally, because sediments contain all sorts of radiometric impurities, very selective radiochemical purification procedures are required.

Measurement of natural ^{32}Si is possible in two ways: 1) detection of beta radiation (radiometry), and 2) measurement of ^{32}Si by accelerator mass spectrometry (AMS) (Morgenstern et al. 2000). The main issue with using AMS for detecting natural ^{32}Si is low ^{32}Si/Si, which ranges between 10^{-12} and 10^{-18}. Only rain and glacier snow and ice have ^{32}Si/Si above the present AMS detection limit of about 10^{-15}, while biogenic silica in sediments, as well as ocean water, river and lake water, and groundwater, have ^{32}Si/Si well below the AMS detection limit and can only be measured radiometrically.

METHOD

Setting

As part of a 1994 study of the sediment budget for the Bangladesh continental shelf (Michels et al. 1998, 2000; Suckow et al. 2001), a sediment core was obtained near the mouth of the Ganges-Brahmaputra river system in the submarine delta forset beds (Figure 1). We have measured ^{32}Si to establish a chronology beyond the dating range of gammaspectrometric methods (^{137}Cs, ^{210}Pb, ^{228}Ra). The terrigenous fraction of the sediment is mostly re-worked from shallower parts of the delta and re-deposited by cyclones and tides. These processes are quasi-continuous and do not mix sediment layers beyond the time resolution of a few years. Once deposited, the sand-silt-clay layers are usually well preserved and are rarely disturbed by bioturbation or other sedimentary processes, which were observed only in the top few cms of the sediment.

Extreme requirements for detection of ^{32}Si were expected for these particular shelf sediments because the concentration of biogenic silica is particularly low (about 1%). Also, the presence of mainly marine diatoms meant that the ^{32}Si specific activity was likely to be only about 10 dpm/kg SiO_2, decreasing over several half-lives down through the core. Counting rates of less than one count per hour were expected.

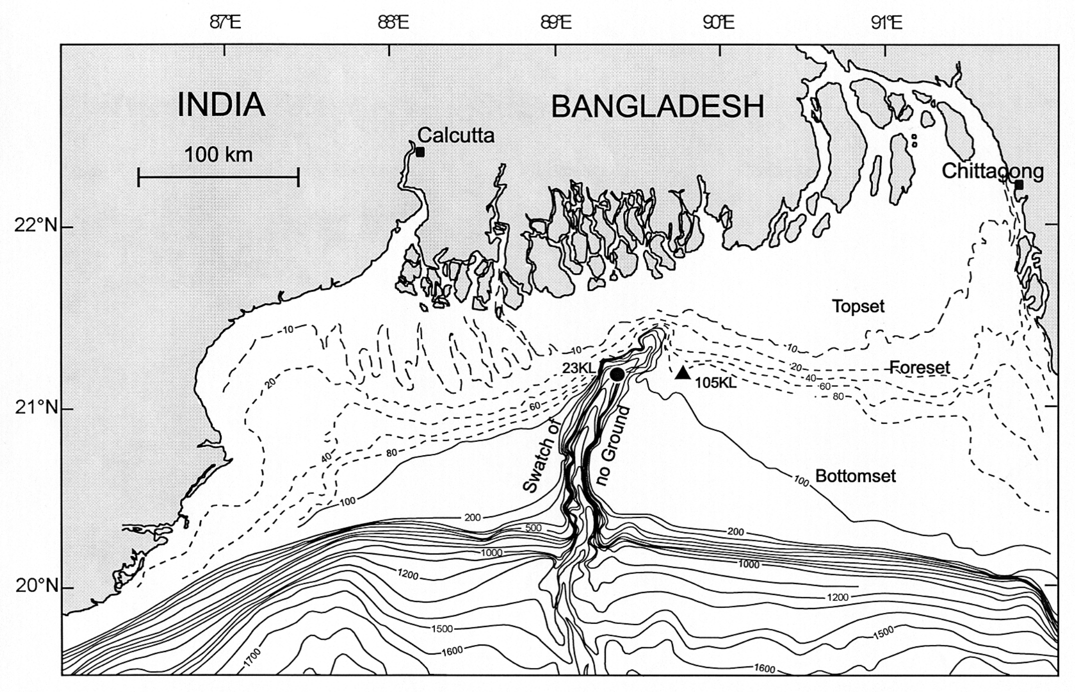

Figure 1 Bathymetric' map of the Bay of Bengal with locations of the coring sites (from Suckow et al. 2001)

Extraction and Purification of the Biogenic Silica

Biogenic silica was extracted from 1 kg sediment samples by dissolution in hot 4M NaOH. No correction was made for additional interfering silica leached from the enclosing sediment. All samples were leached under the same conditions and the correction for varying amounts of additional stable silica—which is difficult to measure (DeMaster 1980)—would be small compared to the uncertainty in the counting statistics for these samples.

After re-precipitation of the silica, the purification procedure described in DeMaster (1980) was followed, but impurities (mainly chromium) were found to be excessive and the silicic acid impossible to completely dissolve in NaOH. Therefore, an alkali fusion in Na_2CO_3 was conducted. After the resulting "cake" was dissolved in water, a small amount of fine brown precipitate was removed by centrifuging and the silica re-precipitated with HCl. The resulting yellow mixture was evaporated to dryness, moistened with HCl, and evaporated again to harden the silica. The salts were dissolved in hot 3M HCl. The silicic acid was easily filtered from the yellow solution and, after washing, appeared to be relatively clean. Samples were then dissolved in NaOH solution and processed through another purification cycle, which included a NaOH dissolution and HCl precipitation, with subsequent washing. The dried silica was then combusted overnight at 900 ˚C, the resulting pure fine white silica being readily soluble in strong NaOH solution.

Radiometric analysis of the extracted insoluble material yielded a count rate per mg of impurity similar to the blank count rate (thought to be from ^{40}K), constant over time. This shows how essential it is to remove even traces of impurities from the silica: approximately 6 g silica was extracted from one kg of sediment, so one mg of impurity has the potential to contribute a blank count rate of about 2 cph. This is intolerable when sample counting rates of fractions of one cph must be measured.

Radiometric measurement

Radiometric analysis of natural ^{32}Si has been achieved in a few laboratories by detecting the beta radiation of its daughter ^{32}P using gas flow counters (Lal and Schink 1960; Somayajulu 1991) and semiconductor detectors (Morgenstern et al. 1995). The difficulties of setting up such extremely low background systems have prevented a wider use of ^{32}Si. We now have introduced commercial scintillation spectrometers (1220 Quantulus) for detection of the extremely low-level activities of natural ^{32}Si, resulting in an improved background (about 2 cph), detection efficiency (about 65%) and measurement stability.

^{32}Si is a β^--emitter (maximum energy 0.225 MeV). However, these β^- events can not be detected due to sample bulkiness and self-absorption. The only practical method for the radiometric measurement of natural ^{32}Si is via its daughter ^{32}P (β^-, maximum energy 1.71 MeV, half-life 14.28 days). In the purified silica sample, ^{32}P grows into secular equilibrium during 2–3 months and can be extracted (milked) with only a few milligrams of carrier phosphorus. Advantages of employing ^{32}P are 1) easy detection of the higher energy β-radiation, 2) small sample size (only a few mg of extract), and 3) unambiguous identification of the ^{32}P-decay curve.

^{32}P was extracted from the silica using procedures similar to those described by Lal et al. (1960). The resulting magnesium pyrophosphate was mixed with a scintillator and measured in a low-activity teflon-vial over several weeks (Figure 2).

RESULTS

Recent (surface) sediment was not available for ^{32}Si analysis, but the initial ^{32}Si specific activity could be deduced for this area from a well-dated sediment layer from core So 126/23KL (Table 1). The age of this sediment layer was gamma-spectrometrically determined to be 39 years (Michels et al. 2000). Decay-correction of the measured 4.9 dpm/kg SiO_2 by 39 years results in an initial ^{32}Si specific activity of 5.9 ± 0.5 dpm/kg SiO_2. This is in good agreement with the initial ^{32}Si specific activity of 5.7 dpm/kg SiO_2 obtained for sediments from the Gulf of California (DeMaster 1980). The atmospheric ^{32}Si deposition into the ocean is expected to be similar for the two locations due to their similar latitude, and the good agreement suggests a relatively uniform input of ^{32}Si and stable silicon into marine sediment from the two different oceanic reservoirs. Application of the initial ^{32}Si specific activity from Bangladesh core 23KL to 105KL is justified because the two locations are in close proximity, and marine diatoms are dominant in both cores. The ^{32}Si specific activity in the bio-

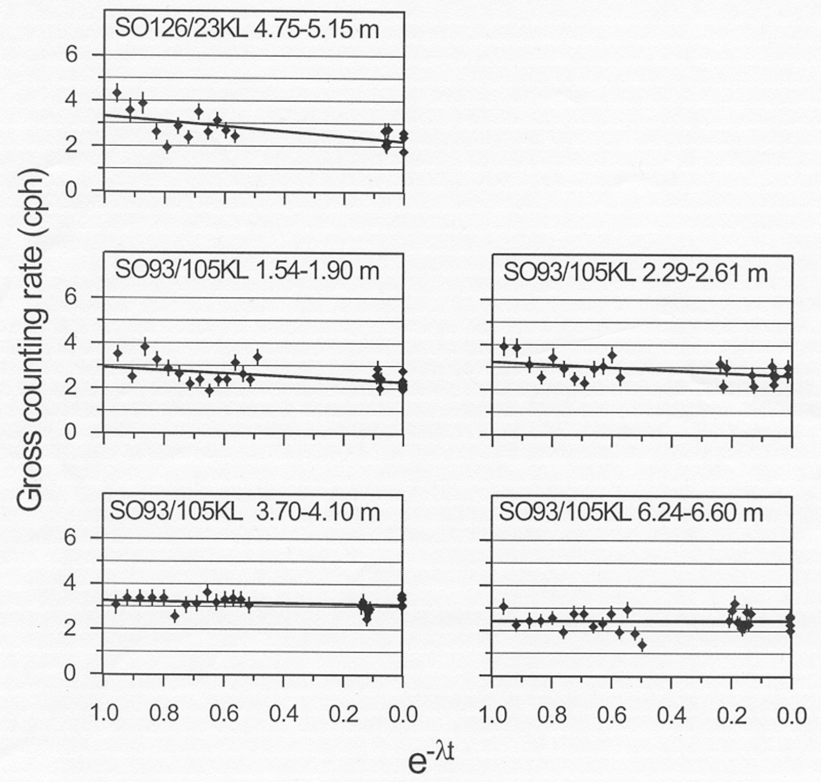

Figure 2 Daily gross β counting rate for sediment samples from the Bangladesh continental shelf. Cph = counts per hour, λ = disintegration constant for ^{32}P = 0.0485 day^{-1}, t = time from milking, error bars represent one sigma counting statistics, full lines are linear fits to the measured data.

genic silica in the sediment does not depend on the water depth above the sediment as the biogenic silica is produced in the surface water. Seasonal ^{32}Si variations are smoothed out for the studied sediment cores as each sampled core section spans several years.

The ^{32}Si age of the sediment below 6 m depth is beyond detection limit, which for this core is 600 yr. This detection limit is somewhat lower than the anticipated 1000 yr because of the extremely low amount of available biogenic silica.

^{32}Si dating results are summarized in Table 1. For the calculation of sediment ages constant ^{32}Si deposition over the past several hundred years was assumed. Note that for ^{32}Si production in the atmosphere, the primary component of the generating cosmic-rays are fast protons, which are relatively unaffected by solar modulation. In addition, no significant increase in ^{32}Si specific activity has been observed so far in sediments deposited at about the time of the Maunder Minimum (minimum solar activity). However, further information on ^{32}Si deposition history is still needed via measurement of well-dated natural archives such as polar glacier ice cores.

DISCUSSION

Using the initial specific activity of 5.9 dpm/kg SiO_2 derived from sediment core So126/23KL we have calculated ^{32}Si ages for the sediment core So93/105KL (Table 1, Figure 3). The ^{32}Si ages correspond well to ^{210}Pb dates from the upper part of the sediments as determined gammaspectrometrically (Suckow et al. 2001). The ^{14}C dates of Suckow et al. (2001) are not interpretable as ages due to the sensitive reaction of the mixtures of dislocated and different old materials containing a variable content of bomb ^{14}C and the uncertain ^{14}C reservoir effect of this environment. The large spread of the ^{14}C dates versus depth demonstrates this.

Table 1 ^{32}Si data for sediments from the Bangladesh continental shelf. ^{32}Si specific activities are decay-corrected to the date of sampling. Ages are calculated using a ^{32}Si half-life of 140 years (Morgenstern et al. 1996).

Depth (m)	Extracted Si (g)	Net ^{32}P counting rate (cph)	^{32}Si specific activity (dpm/kg SiO_2)	Age (years)
Sediment core So126/23KL, November '97 (21°11.39′N, 89°46.99′E, water depth 80 m)				
4.75–5.15	8.32	1.12 ± 0.09	4.90 ± 0.43	39
Sediment core So93/105KL, February '94 (21°11.21′N, 89°23.41′E, water depth 564 m)				
1.54–1.90	6.09	0.75 ± 0.07	4.60 ± 0.44	53 ± 20
2.29–2.61	7.80	0.61 ± 0.08	2.93 ± 0.39	144 ± 28
3.70–4.10	5.98	0.17 ± 0.08	1.01 ± 0.46	360 ± 95
6.24–6.60	6.16	–0.02 ± 0.07	–0.12 ± 0.40	$600\,^{+\infty}_{-100}$

The linear ^{32}Si age profile between 50 and 400 years (Figure 3) suggests that the sedimentation rate was relatively constant over that time, 0.70 ± 0.20 cm/yr. However, the linear fit does not extrapolate into the origin (zero age at depth zero). Connecting the youngest ^{32}Si age to the origin results in a much steeper slope over the past 50 years with a mean deposition rate of 3.1 ± 0.8 cm/yr, in good agreement with ^{210}Pb data for that time period (see Figure 3). The ^{32}Si data suggest, then, that the sedimentation rate has increased significantly over the past fifty years. Although only a relatively few ^{32}Si dates are available, the agreement in the overlapping time range with the ^{210}Pb dates confirms the robustness of the ^{32}Si dating method.

The higher age versus depth gradient for the upper part of the profile cannot be explained by bioturbate homogenization, which in this core affects only the top few cms. Also, compaction of the sediment with depth is negligible because the wet bulk density increases by only 5% between the surface and the deepest layers. The higher age versus depth gradient in the upper sediment may therefore be interpreted as a four-fold increase in sedimentation rate over the past 50 years, caused by an increased sediment load in the rivers due to increasing human colonization within the rivers' drainage basins.

CONCLUSIONS

A new detection method for ^{32}Si with improved sensitivity allows for the measurement of natural ^{32}Si in sediments. We have measured specific ^{32}Si activities in a sediment core from the shelf of Bangladesh, the initial ^{32}Si specific activity being deduced from a well-dated core nearby, and the data being converted into ^{32}Si ages. ^{32}Si and ^{210}Pb dates are in good agreement for the past 50 years.

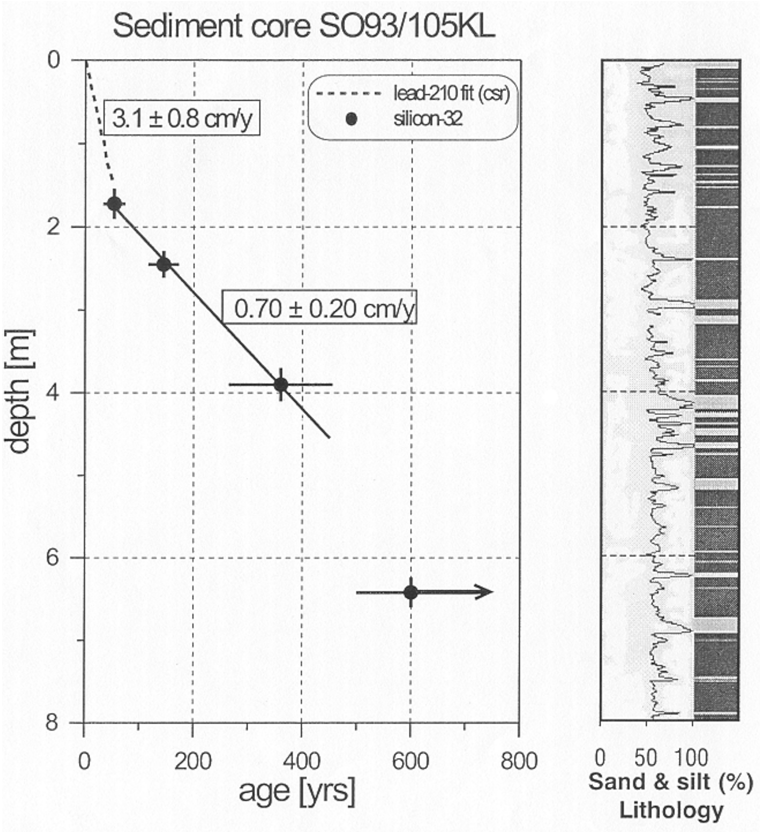

Figure 3 ^{32}Si age depth profile for sediment core So93/105KL from the Bangladesh continental shelf. Included is the sand+silt log (from Michels et al. 1998). The sedimentation rates are derived from the ^{32}Si data (see text). The dotted line between 0 and 50 years is the age fit from the ^{210}Pb dates yielding sedimentation rate 2.6 cm/yr (Suckow et al. 2001) in good agreement with the ^{32}Si dates.

The ^{32}Si data suggest relatively constant sedimentation rate over the time range 50–400 years, but significantly increased sedimentation rate over the past 50 years. The studied core from Bangladesh represents extremely difficult analytical conditions for ^{32}Si dating. Lake sediments and also ocean sediments with higher concentrations of biogenic silica would be expected to give better counting statistics due to more available ^{32}Si.

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