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^{10}Be meltwater signal in Orca basin sediments, Gulf of Mexico

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Abstract. An increase in the cosmogenic beryllium-10 content of the Orca basin sediments due to the flooding of the Gulf of Mexico (GM) by meltwaters during the late Wisconsin interglacial is reported. A strong negative correlation ($\gamma = -0{\cdot}99$) between $\delta^{18}O$ (in the range of $-1{\cdot}5‰$ to $+0{\cdot}5‰$) and ^{10}Be/Al ratio is seen. During intense flooding reflected by a decrease in $\delta^{18}O$ by $\sim 2‰$, this correlation may not hold as some of the sediments with low ^{10}Be/Al ratio and deposited on the shelf and slope regions of the GM during the earlier glacial period would also be washed into the basin. The deposited sediment would then be a mixture with a ^{10}Be/Al ratio lower than expected from the correlation.

Keywords. Meltwater; beryllium-10; Gulf of Mexico; cosmic rays.

1. Introduction

Cosmogenic beryllium-10 (half life = 1·5 Ma) can be a potential tracer for deciphering meltwater flooding of the oceans during interglacial times in view of its congenial seawater chemistry and the fact that its measurement in natural samples can now be achieved with high sensitivity by Accelerator Mass Spectrometry (AMS). The basic philosophy behind this application, as suggested by Somayajulu (1977), is that the most concentrated solutions of ^{10}Be on earth are rain and (melted) snow/ice, the latter accumulated for long periods during glacial times. During interglacial periods the ice/snow meltwater rich in ^{10}Be flooded the oceans and the ^{10}Be spike got removed by detrital material, principally clays (that are enriched in Al), transiting through the water column to form the sediment, in times shorter than the mixing times of the oceans viz., $\sim 10^3$ years (McHargue and Damon 1991). To detect this signal, one should look for oceanic areas which were subjected to intense meltwater flooding in the past and measure ^{10}Be and Al in their sediments as a function of $\delta^{18}O$ which happens to be the indicator of meltwater inputs (Emiliani 1955; Imbrie and Imbrie 1979). In the Arctic Ocean, increase of ^{10}Be in sediments deposited during interglacial times has been reported recently (Eisenhauer *et al* 1994; Somayajulu *et al* 1996). In the Antarctic continental margin sediments from circumpolar region (southern ocean) too increase. In ^{10}Be concentrations during interglacials was reported (Frank *et al* 1995) but the increase was attributed to high biological productivity prevailing during warmer periods. It is very likely that high biological productivity results in a more efficient scavenging of clays that are more enriched in meltwater ^{10}Be during interglacials.

Deep sea sediments of the Orca basin in the northern GM (figure 1) contain a more complete history of the Lawrentide ice sheet melting because the GM was flooded by its meltwaters during the Wisconsin interglacial (Emiliani *et al* 1975; Kennett and Shackleton 1975; Leventer *et al* 1983). This $\sim 400\ km^2$, anoxic basin with hypersaline waters

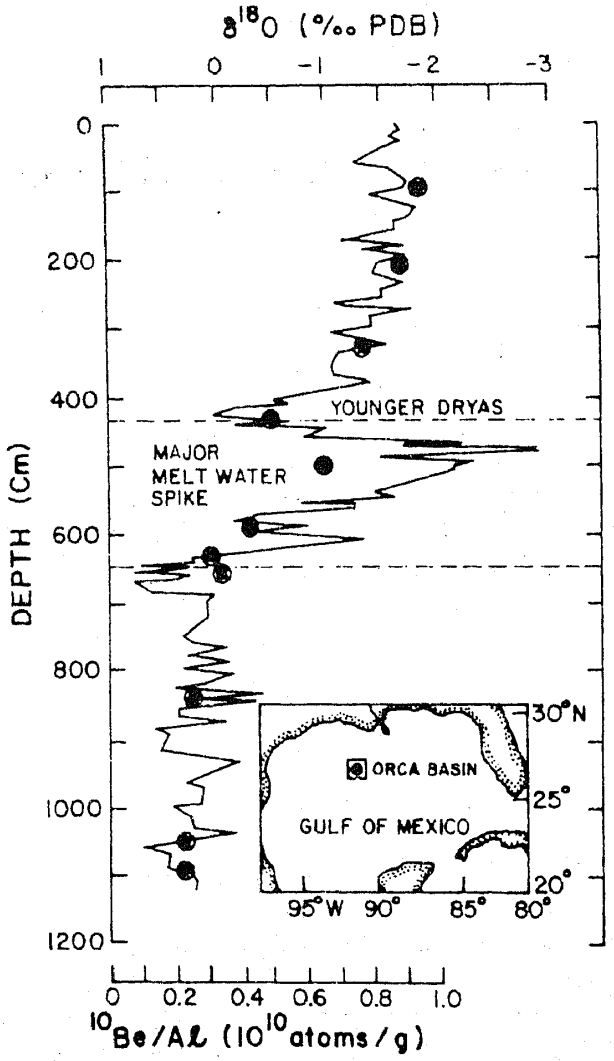

Figure 1. The complete $\delta^{18}O$ depth profile along with the $^{10}Be/Al$ ratios (shown as encircled black dots) in core EN32 PC6 from the Orca basin. The location of the basin in GM is shown in the inset. The horizontal dashed lines indicate the meltwater flooding period (Kennett *et al* 1985).

filling the bottom ~ 200 m of its water column (Shokes *et al* 1977; Kennett *et al* 1985) and its organic carbon rich sediments (Sheu and Presley 1986) will be devoid of bioturbation and hence ideally suited for the detection of ^{10}Be spike(s). In addition, the sedimentation rates are high as a result of its proximity to the continental shelf and slope regions (Leventer *et al* 1983; Kennett *et al* 1985; Broecker *et al* 1988, 1990) which facilitates high resolution paleoceanographic/ paleoclimatic measurements.

Eleven samples from the piston core EN32 PC6 (location: 26° 56·8′N, 91 21′W; water depth = 2280 m) from the Orca basin, GM (figure 1) representing the last glacial maximum (LGM) followed by the Wisconsin interglacial flooding as evidenced by $\delta^{18}O$ (Emiliani *et al* 1975; Kennett and Shackleton 1975; Leventer *et al* 1983) were analysed for ^{10}Be. A negative correlation ($\gamma = -0{\cdot}88$) between $\delta^{18}O$ and ^{10}Be was obtained (Somayajulu *et al* 1991). However, due to problems associated with the earlier ^{14}C-based sedimentation rates of EN32 PC6, and the assertion by Broecker *et al* (1988) that a portion of this core representing the peak flood period was missing, it was not

Table 1. ^{10}Be, δ^{18}O, $CaCO_3$, Fe and Al in the Orca basin core EN32 PC6.

Sample code	Depth (cm)	$CaCO_3^+$ (%)	$\delta^{18}O^+$ (‰ PDB)	$^{10}Be^+$ (10^8 atom/g)	Al* (%)	Fe* (%)	^{10}Be/Al (10^{10} atom/g)
E1	100–105	16·2	−1·51	3·40	3·47	1·88	0·98 ± 0·12
E2	218–220	13·2	−1·41	3·46	3·84	2·17	0·90 ± 0·14
E3	338–340	13·6	−1·11	3·85	4·87	2·44	0·79 ± 0·09
E4	440–442	9·0	−0·64	3·03	5·70	2·88	0·53 ± 0·08
E5	495–500	11·6	−1·98	3·70	5·54	2·71	0·67 ± 0·08
E6	594–596	9·1	−0·29	2·56	5·51	2·68	0·46 ± 0·06
E7	630–632	8·6	0·23	1·99	5·86	2·71	0·34 ± 0·05
E8	670–672	8·6	0·72	2·46	6·40	2·97	0·38 ± 0·05
E9	850–855	10·3	0·35	1·90	6·91	3·34	0·27 ± 0·03
E10	1000–1004	7·4	0·42	1·58	6·71	3·32	0·24 ± 0·03
E11	1088–1092	8·4	0·51	1·71	7·08	3·49	0·24 ± 0·03
Interglacial sediments (average of samples E1 to E3)							
IG	0–340	14·3	−1·34	3·57	4·06	2·16	0·89 ± 0·11
Glacial sediments (average of samples E9 to E11)							
G	850–1092	8·7	0·43	1·70	6·90	3·38	0·25 ± 0·03

$^+$From Somayajulu *et al* 1991.
*Errors on metal concentrations are ± 5%.

possible to unequivocally relate the ^{10}Be increases with meltwater injections. Other plausible explanations such as (**i**) focussing effect and (**ii**) erosion of the then existing ^{10}Be enriched sediments in the Mississippi drainage basin were evoked to explain the data (Somayajulu *et al* 1991). Since the $CaCO_3$ contents of the samples are small (range = 7·4%–16·2%, mean = 10·5 ± 3·4%; table 1) the data were not taken on a $CaCO_3$ free basis. The deposition rates of ^{10}Be derived using the ^{14}C-based sedimentation rates given by Broecker *et al* (1988) were used to explain the ^{10}Be variations as a function of δ^{18}O (see figure 2).

Later Broecker *et al* (1989, 1990) dated additional sample(s) of the same core and concluded "that no hiatus existed in EN32 PC6 and that its accumulation was continuous" as observed earlier by Kennett *et al* (1985). All the AMS ^{14}C data put together yield an accumulation rate of ~45 cm/10^3 yr for EN32 PC6. This suggested that it is possible to delineate the meltwater-injected ^{10}Be signal(s) provided one can normalize the ^{10}Be content of the samples to their clay content (size $\leqslant 4\,\mu$m, Grim 1953) which is the main constituent of detrital matter that adsorbs ^{10}Be from seawater. A significant part of this fine fraction with large surface area consists of clay minerals (Grim 1953; Whitten and Brooks 1972) which are hydroxy alumino-silicates that effectively adsorb reactive elements such as Be, Al, Fe from seawater (Sharma *et al* 1987). Fe cannot be used for normalization as its concentration in marine sediments is affected by redox chemistry – a problem that does not exist for Be and Al. In some deep sea red clays, it has been shown that Al content increased with decreasing size (Goldberg and Arrhenius 1958) and the best method of ascertaining clay content is through Al measurements. It should be added here that presenting ^{10}Be concentration on $CaCO_3$-free-basis is not the right method as all non-calcareous materials (e.g., sand fraction) do not contain clays (Al). Also sediments, from near-coastal regions like GM will have a sizeable fraction of feldspars, pyroxenes etc., mostly in the silt size range

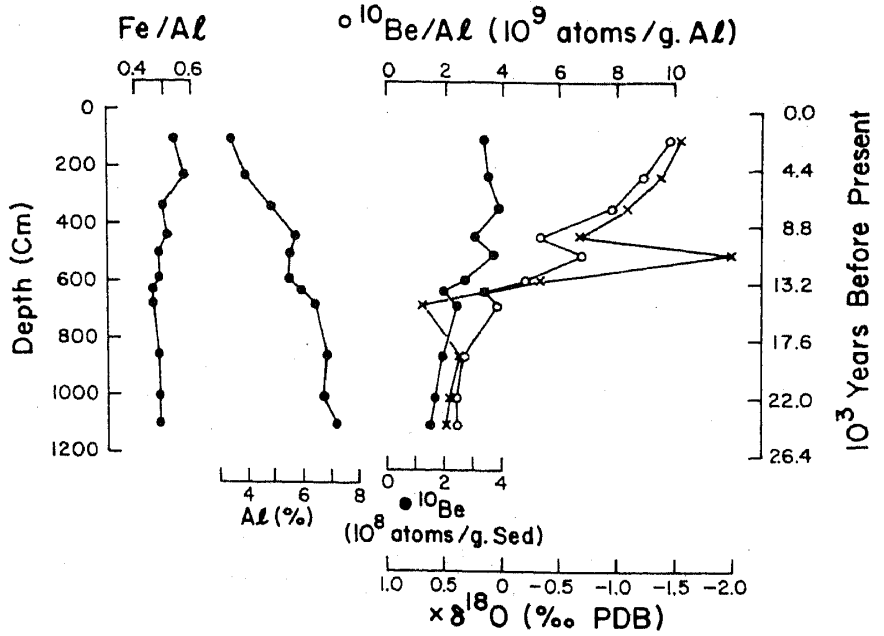

Figure 2. On the left are shown the Al and Fe/Al variations with depth. On the right side are shown the variations of ^{10}Be, ^{10}Be/Al and δ^{18}O in the samples analysed. It is clear that ^{10}Be/Al variations show a more pronounced correlation with δ^{18}O than with ^{10}Be (Somayajulu *et al* 1991). Notice that the δ^{18}O scale is reversed to show the effect similar to the ^{10}Be/Al increase.

which will lower the ^{10}Be content. This is known: the shelf and slope sediments have on an average $\sim 10^8$ ^{10}Be atoms/g whereas the deep sea red clays contain $\sim 10^9$ atoms/g (Brown 1984).

2. Methodology

Since the earlier samples were exhausted, small amounts of the same-depth-samples of EN32 PC6 were procured from the University of Rhode Island. These were analysed for Al and Fe by atomic absorption spectrophotometry (Sarin *et al* 1979) and the data are presented in table 1 together with that on $CaCO_3$, ^{10}Be and δ^{18}O (Somayajulu *et al* 1991).

3. Results and discussion

The location of the Orca basin, δ^{18}O variation (in G. ruber), and of the ^{10}Be/Al ratio as a function of depth in core EN32 PC6 are shown in figure 1 from which it is evident that the pattern of variation of ^{10}Be/Al ratio as a function of depth is quite opposite to that of δ^{18}O. This is what is expected if ice-meltwater floods the GM. A plot of ^{10}Be/Al ratio as a function of δ^{18}O is shown in figure 3 for which the best fit-line is obtained taking the errors into consideration (Williamson 1968). The regression equation is:

$$^{10}\text{Be/Al}(10^{10}\text{atoms/g}) = -(0{\cdot}34 \pm 0{\cdot}03)\,\delta^{18}\text{O}\ (‰) + (0{\cdot}39 \pm 0{\cdot}02) \qquad (1)$$

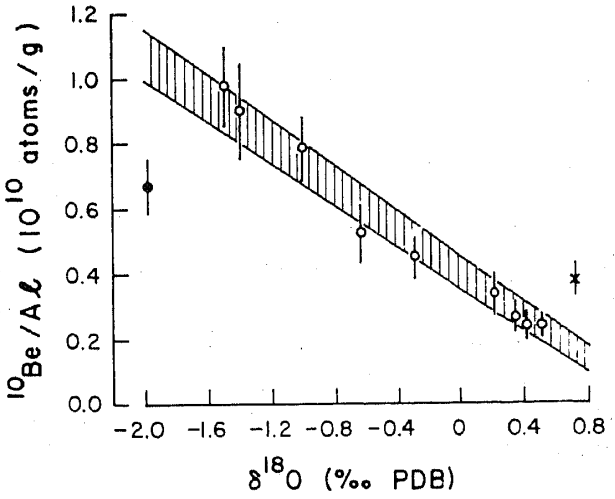

Figure 3. ^{10}Be/Al ratio versus δ^{18}O plot for EN32 PC6. The shaded band represents the best-fit-line with errors. Sample E5, shown as a black dot ($\delta^{18}O = -1{\cdot}98‰$), and E8 (denoted by *X*) are not used in the regression analysis. See text for discussion.

with $\gamma = -0{\cdot}99$. This expected negative correlation is for nine out of the eleven data points (table 1, figure 3). It must be added here that even if all the data points are considered γ is only slightly less at $-0{\cdot}89$. The two points excluded are: (i) sample E5 ($\delta^{18}O = -1{\cdot}98‰$) representing the peak meltwater injection period with a ^{10}Be/Al = $(0{\cdot}67 \pm 0{\cdot}08) \times 10^{10}$ atoms/g and (ii) sample E8 ($\delta^{18}O = 0{\cdot}72‰$) representing the period just before the meltwater injection which according to Kennett *et al* 1985, is represented by the 430–640 cm section of the core EN32 PC6 (figure 1, table 1). The reasons for the exclusion of these two samples are as follows: in the Orca basin foraminifer G. ruber, showed increase in frequency with warming as indicated by decreasing $\delta^{18}O$ values right from the beginning of the meltwater discharge (Kennett *et al* 1985). This pattern was not followed in the last glacial maximum (LGM) times, the most glaring departure occurred just before the meltwater discharge represented by sample E8. The $\delta^{18}O$ of this sample is more positive compared to the other samples E9 to E11 covering the LGM. This is also seen in the ^{10}Be/Al ratio in E8 which is $[(0{\cdot}38 \pm 0{\cdot}05) \times 10^{10}$ atoms/g] compared to the LGM samples measuring 0·24 to 0·27. It is noted by Broecker *et al* (1989) that the pink variety of G. ruber which occurs in the GM sediments along with the white variety has $\delta^{18}O$ values 1‰ lower than that of the latter during glacial and Younger Dryas times. It is remotely possible, therefore, that sample E8 could have had a few individuals of the white variety justifying its exclusion from the regression.

In the case of sample E5, the expected/predicted (from equation 1) ^{10}Be/Al is $(1{\cdot}07 \pm 0{\cdot}07) \times 10^{10}$ atoms/g which, within the errors of measurement is equal to that measured in the top sample, E1, with a $\delta^{18}O$ of $-1{\cdot}51‰$ (table 1). This means that the ^{10}Be/Al ratio and $\delta^{18}O$ in the Orca basin sediments have been high and low respectively as recently as ~ 2 ky ago. This could be due to sediments with high ^{10}Be/Al ratios in the continental margins of GM. Indeed Brown *et al* (1987), who measured surface sediments from the inner and outer shelf regions of GM (water depths $\leqslant 100$ m), found ^{10}Be concentrations averaging $(3{\cdot}62 \pm 0{\cdot}94) \times 10^8$ atoms/g. Assuming that the Al contents of the shelf sediments are similar to the top sections viz., samples E1 to E3 of EN32 PC6 (mean Al = 4·06%, table 1), the ^{10}Be/Al ratios average $(0{\cdot}89 \pm 0{\cdot}27) \times 10^{10}$ atoms/g in very good agreement with the ratio of the top sample, E1 (table 1).

The measured low ^{10}Be/Al ratio of $(0{\cdot}67 \pm 0{\cdot}08) \times 10^{10}$ atoms/g in sample E5, (which represents the peak-flood-period) compared to the expected ratio of $(\geqslant 1{\cdot}07 \pm 0{\cdot}07) \times 10^{10}$ atoms/g, can be explained using a two component model for sediment deposition in the Orca basin during the peak-flood period. The two components are: (i) sediments that were draining into Orca basin during $\sim 13{\cdot}5 - 11{\cdot}0$ ky ago which were having the expected ^{10}Be/Al ratio, $(1{\cdot}07 \pm 0{\cdot}07) \times 10^{10}$ atoms/g. These sediments are assumed to resemble in composition the ones that have been deposited since the end of the Younger Dryas period viz., ~ 10 ky BP. These are termed interglacial sediments whose composition is represented by the average of sample E1 to E3 (table 1) and (ii) sediments deposited during the glacial (LGM) times (represented by the average of samples E9 to E11, table 1). The glacial sediments are enriched over their interglacial counterparts in Al and Fe by a factor of 1·6, depleted in ^{10}Be by a factor of ~ 2, and in ^{10}Be/Al ratio by a factor of ~ 4(table 1). Using the relation:

$$C_{IG}X + (1 - X)C_G = C_{PF}, \tag{2}$$

where C is the concentration/ratio and IG, G and PF represent interglacial, glacial and peak flood periods respectively. X is the fraction of interglacial sediment and $(1 - X)$ that of glacial sediment. Using $CaCO_3$, Al, Fe and ^{10}Be/Al ratio, one obtains $\sim 50\%$ for both X and $(1 - X)$ which means that during the peak flood period represented by sample E5, approximately equal amounts of sediments of the interglacial type the clay component of which had adsorbed a proportional amount of ^{10}Be from seawater such that the ^{10}Be/Al was 1·07 (equation 1) and the then existing glacial sediments from the continental margins of GM which have a ^{10}Be/Al ratio of $0{\cdot}25 \times 10^{10}$ atoms/g and δ^{18}O of 0·43‰ and (table 1) were eroded and got mixed up. This mixture represented by sample E5 is therefore lower in its ^{10}Be/Al ratio than the one expected from the correlation (equation 1). It is very likely that during periods of intense flooding, as had happened in the GM during the Wisconsin interglacial, the normal/expected relation between ^{10}Be and δ^{18}O may not hold.

Despite the downcore increase of Al, the Fe/Al ratio remained remarkably constant (figure 2) in the core indicating that the overall character of the detrital material depositing in the Orca basin did not change during the time period represented by the core viz., ~ 25 ky. Only the clay fraction (Al), which is enriched in Fe has increased by a factor of 1·70 (table 1).

Using $CaCO_3$ to derive the relative amounts of the two components poses two problems which need explanation. Both the ^{14}C ages and δ^{18}O are measured on the biogenic carbonate. A fifty-fifty mixture of interglacial and glacial sediments would imply that the measured ages as well as δ^{18}O are not the real values representing the peak-flood-period, as the glacial carbonate component would have increased both parameters. One way of getting around the problem is to assume that foraminifera in the previously existing glacial sediments on the shelf and slope regions would have broken down during the enormous flooding eposide (Wisconsin interglacial) whereas the ones formed in the surface ocean during that period were unaffected during deposition. Since the ^{14}C ages as well as δ^{18}O (on G. ruber) were determined on hand-picked individuals, the chances of contamination from glacial sediments would be minimal or negligible. Previous ^{14}C dating of sedimentary organic carbon of GM (Leventer *et al* 1983) could have had such a problem as the ages were older. That hand-picked forams do give the right signal can be established from the δ^{18}O data. If

a fifty-fifty mixture of forams was taken, the δ^{18}O of sample E5 would have been much lower than the measured value of $-1{\cdot}98‰$ (table 1). Hence the assumption that only unbroken foraminifera represent the ones that formed in the Gulf of Mexico waters during the peak flood period, is not unreasonable.

The Younger Dryas event is well documented in the Orca basin sediments (11 to 10 k Yr BP, Flower and Kennett 1990; Kennett 1990) and there appears to be the expected decrease as the sample E4 representing this period shows the expected decrease in the ^{10}Be/Al ratio relative to the ratios of samples E3 and E5 (table 1, figures 1 and 3). While this decrease is marginal, it is significant enough to warrant this type of study in other oceanic areas that were subjected to intense meltwater inputs. These are the Arctic, the Gulf of St. Lawrence and the western north Atlantic, the Mediterranean Sea, the Bay of Bengal and the southern ocean. As mentioned in § 1, Eisenhauer *et al* (1994) did find increases in ^{10}Be in Arctic sediments during interglacials and Frank *et al* (1995) made a similar observation in sediments from the continental margins of Antarctica. Measurements of ^{10}Be both in Antarctic ice cores (Raisbeck *et al* 1987) and in Pacific Ocean sediments (Lao *et al* 1992), indicate that its deposition rate had been high during glacial periods by at least 25%. The causes could be several but this increase in the past glacier-melts should result in good ^{10}Be/Al signals in the oceanic regions mentioned above.

In conclusion, it can be said that ^{10}Be/Al ratio is a more reliable indicator of past meltwater spikes compared to just ^{10}Be concentration (Somayajulu 1995). Whereas the former is independent of sedimentation rate and other variations in the sedimentary processes, the latter is dependent on them. It is likely that 6M HCl leach, which brings into solution $\geqslant 90\%$ of the ^{10}Be contained in sediment (Kharkar *et al* 1963; Amin *et al* 1966) that was adsorbed from seawater and also a significant amount of the dissolved Al from seawater is a better method over the total dissolution technique. Whereas δ^{18}O shows faunal response to warming, flooding, i.e., lower salinities ^{10}Be/Al represents the corresponding change in the clay (detrital) matter. Simultaneous measurement of these two in meltwater affected oceanic areas will lead to a better understanding of the meltwater spikes and associated phenomena because the former indicates changes in both temperature and salinity whereas the latter depends on salinity alone.

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