

# Radiocarbon

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## <sup>14</sup>C AGE CORRECTIONS IN ANTARCTIC LAKE SEDIMENTS INFERRED FROM GEOCHEMISTRY

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**ABSTRACT.** Sediment from Lake Boeckella, Antarctic Peninsula, is richer in Ca, Cd, Cu, P, Sr and Zn than that of six other lakes in the area. The elements originate from Adélie penguin (*Pygoscelis adeliae*) guano on the lake shores. Changing Cu and P concentrations in the lake sediment are used as a proxy for penguin influence on the lake sediment from ca. 5850 BP to present. A <sup>14</sup>C dating model suggests that the <sup>14</sup>C correction factor in the lake sediments depends on the penguin proxy, the apparent age of the penguin guano and the amount of particulate carbon originating from the carbon-bearing shales in the watershed. Glacial meltwater and dissolved carbonates do not contain enough "old" carbon to contribute significantly to the correction factor. Ages corrected with the <sup>14</sup>C dating model agree with the depth vs. age curve based on independently <sup>14</sup>C-dated tephra horizons. The reservoir effect has been constant since at least 5800 BP, implying long-term stability of the currents and water masses in the area. The existing chronology for Lake Boeckella has been recalculated. The period of glacial advance, previously thought to have culminated at 5000 BP, is now thought to have culminated at 4700 BP; deglaciation of the area is thought to have occurred at 6300 BP instead of 8680 BP.

### INTRODUCTION

Lake sediments from the Antarctic Peninsula and the surrounding islands were sampled in 1987 during the RV *Polarstern* expedition, ANT VI, and in 1989, during the 1988/89 SWEDARP expedition (Karlén *et al.* 1988; Björck *et al.* 1989) to reconstruct Holocene climate of the area (Zale and Karlén 1989). A problem with Antarctic <sup>14</sup>C dates (*cf.* Zale and Karlén 1989; Björck *et al.* 1991) stems from the marine reservoir effect in the sea around Antarctica and the abundance of fossil carbon in the bedrock. (The term *reservoir effect* refers to the fact that marine plants and animals yield "old" <sup>14</sup>C dates because deepwater wells up in the area, bringing "old" CO<sub>2</sub> to the surface (*cf.* Omoto 1983; Stuiver and Braziunas 1985; Stuiver, Pearson and Braziunas 1986).)

Lake Boeckella in Hope Bay (Fig. 1) displays the following three characteristics: 1) The uppermost deposits show <sup>14</sup>C ages of ca. 2100 BP with no evidence for erosional loss of recent deposits or of non-deposition of sediment. A <sup>14</sup>C correction factor of 2100 yr, based on the age of the modern sediment, was previously applied to the entire core (Zale and Karlén 1989). 2) Unlike most lakes in the area, Boeckella is eutrophic because of the input of nutrients from the nearby Adélie penguin (*Pygoscelis adeliae*) rookery (Hansson 1990, Izaguirre *et al.* 1993). 3) Lake Boeckella has a tephra chronology, independently <sup>14</sup>C-dated at other sites (Björck, Sandgren and Zale 1991). Lake Boeckella dates lack reliability because the correction factor's variation with depth is unknown. Dating accuracy is important in Antarctica, in general, as evidence for environmental change is scarce.

The aim of this study is to test whether inputs of "old" carbon have influenced <sup>14</sup>C dates and to estimate the correction factor at different depths of the Lake Boeckella sediment. The hypothesis is that the correction factor depends mainly on the variable influx of "old" marine carbon from the penguin rookery. The correction factor is used to convert <sup>14</sup>C ages to "true" <sup>14</sup>C ages when sediment containing a mixture of "recent" and "old" carbon is dated. "True" <sup>14</sup>C ages refer to the standard NBS oxalic acid <sup>14</sup>C time scale (*cf.* Olsson 1986) and include neither bomb-carbon nor fossil-fuel correction.

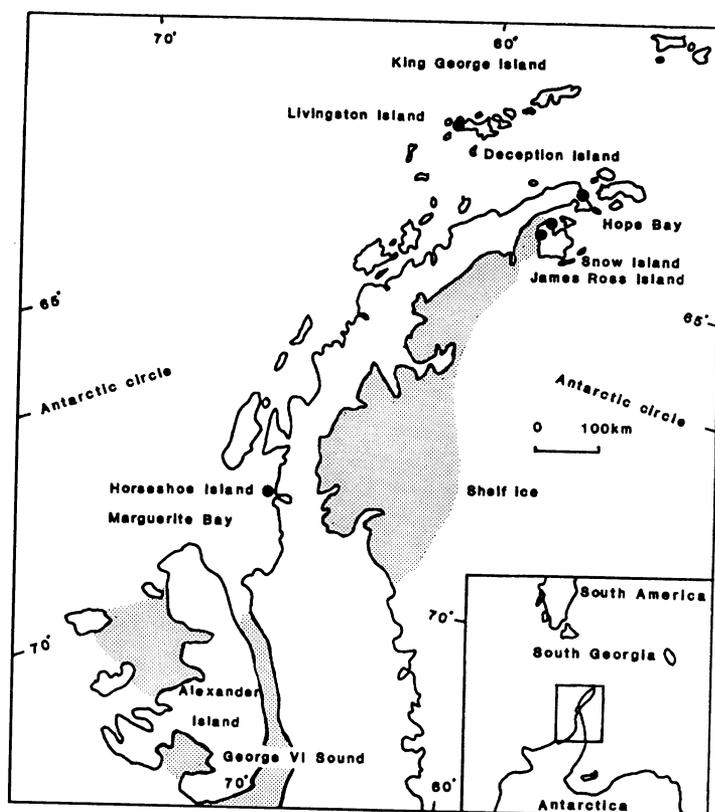


Fig. 1. The Antarctic Peninsula area. • = sampled lakes.

Results will be compared with the tephra chronology, and may shed light on dating difficulties in Antarctica.

Lake Boeckella is a small (0.06 km<sup>2</sup>), eutrophic, freshwater lake with a maximum depth of 9 m, ca. 800 m south of the Esperanza station in Hope Bay at 45 m asl (Fig. 1). Glacial meltwater flows into the lake. A large Adélie penguin rookery, which had ca. 200,000 adults in 1987, borders the lake to the northwest. (Adélie penguins prey mainly on euphausiids (krill) and marine crustacea (Culik 1987), including larval fish, cephalopods and other crustaceans (Watson 1975).) The bedrock in the area consists of Upper Paleozoic marine sediments and Middle Jurassic to Lower Cretaceous volcanic rocks (British Antarctic Survey 1979).

## METHODS

### Field Work

Lake Boeckella sediment samples were collected during the *Polarstern* expedition with a Livingstone-type corer (Zale and Karlén 1989). During the SWEDARP expedition, Björck *et al.* (1989) collected sediment cores from six lakes on the Antarctic Peninsula and surrounding islands. Sediment increments from these cores were analyzed to obtain reference or background concentrations of different elements without the influence of penguins or other marine animals. Water was sampled in both the inlet and outlet of Lake Boeckella to study relations among ionic concentration of inflow water, outflow water and sediment. Four samples of penguin guano were collected from each of two

Adélie penguin rookeries, one in Hope Bay and one at Penguin Point, Snow Island (Fig. 1) during the latter expedition to compare guano and sediment compositions.

### Chemical Analyses

As it is not possible to measure directly the amount of carbon in sediment originating from penguin guano, I took an indirect approach. I assumed that a high concentration in the sediment of one or more elements from the penguin guano resulted from guano washing into the lake. Such element(s) could serve as proxy variable(s) for the penguin influence on the lake sediment (penguin proxy). Sixteen samples from the Lake Boeckella sediment core and 3 widely spaced stratigraphic horizons from each sediment core from the 6 reference lakes were analyzed for Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sc, Si, Sn, Sr, Ti, Zn, Zr, V, W and Y. The samples were leached with a mixture of HNO<sub>3</sub> and HCl in a heated, ultrasonic bath and filtered prior to the ICP-AES analysis of the filtrate; they were kept in a freezer prior to analysis. Five of the 16 Lake Boeckella samples underwent separate analysis for Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MgO, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Ba, Be, Co, Cr, Cu, La, Mo, Nb, Ni, Pb, Sc, Snb, Sr, V, W, Y, Yb, Zn and Zr. These samples were melted with LiBO<sub>2</sub> and then dissolved in HNO<sub>3</sub> prior to ICP-AES analysis. Because of the low sample weights from Lake Boeckella, loss on ignition (LOI) (Zale and Karlén 1989) was used to estimate carbon content (Håkanson and Jansson 1983).

Water samples were analyzed for Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, V and Zn. The water samples were filtered prior to ICP-AES analysis. Penguin guano samples were kept frozen until analyzed for Al, As, Ba, C, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sr, Ti, V and Zn. The samples were dried and then dissolved in HNO<sub>3</sub> and HCl in closed Teflon vessels in a microwave oven prior to ICP-AES analysis. Concentrations of all substances are expressed as percent or ppm of the dry weight, except for water analyses, which are expressed as mg liter<sup>-1</sup> or µg liter<sup>-1</sup>.

The following criteria were established to identify elements to be used as proxies for the penguin contribution to the sediment carbon pool in Lake Boeckella: 1) They must originate from the penguin guano and be present in the sediment in concentrations above background concentrations; 2) they must be chemically stable in the sediment.

### Background Element Concentrations

Background concentrations are mean element concentrations in the sediments from six lakes (18 samples) in the Antarctic Peninsula area that are not influenced by marine animals. Background levels in sediment of polluted lakes are often obtained from mud in the bottom of the core, deposited in pre-industrial times (Bruland *et al.* 1974; Kemp *et al.* 1976; Håkanson and Jansson 1983). This method alone is not suitable for Lake Boeckella, because the time of its penguin rookery establishment is unknown. However, it is used to "correct" the "reference lake method", as no substance should show a statistically significant lower level in any sample of the Lake Boeckella core than the background level. If it does, Lake Boeckella has an anomalously low concentration of that element.

### Radiocarbon Dating

All <sup>14</sup>C ages were measured at Laboratoriet för Isotopgeologi in Stockholm and were published previously (Zale and Karlén 1989). The penguin guano samples were not dated, mainly because of their very low dry weight and the lack of thick guano deposits in Hope Bay.

I developed a mathematical model that incorporates the amount and "age" of the carbon coming into the lake to calculate the "true" <sup>14</sup>C age of the sediment. Lake Boeckella receives carbon from four

main sources: 1) particulate carbon from watershed rocks and soils; 2) penguin guano; 3) dissolved "old" atmospheric CO<sub>2</sub> in the inflowing glacier meltwater and dissolved carbonates in other inflowing water; 4) atmospheric CO<sub>2</sub>.

I assumed that: 1) the particulate carbon originating from the watershed soil/bedrock is proportional to the amount of minerogenic material in the sample and has an infinite apparent age. This assumption is supported by the presence of fossil-bearing shales and mudstones containing carbon in the watershed (Bibby 1966); 2) the amount of carbon originating from penguin guano is proportional to the penguin proxy and of finite apparent age; 3) the apparent age of the water reaching the lake has been constant through time. Carbon originating from meltwater is mixed both with atmospheric CO<sub>2</sub> as the meltwater flows down to the lake, and with water containing dissolved carbonates from bedrock. This carbon makes up the rest of the carbon in the sediment, the apparent age of which is a function of the amount and age of the meltwater (finite apparent age), the amount of dissolved carbonates (infinite apparent age) and the amount of atmospheric carbon (apparent age zero) mixed in.

The "true" <sup>14</sup>C age of a sample can be calculated with the formula

$$a_1 = j_1 - R_{a1} - R_{g1} \quad (1)$$

where

- a = "true" <sup>14</sup>C age in years BP;
- j = <sup>14</sup>C age of the dated sample in years BP;
- R<sub>a</sub> = correction factor of the autochthonous carbon in years;
- R<sub>g</sub> = correction factor of the penguin guano in years.

The subscripts denote the sample number starting with the sample closest to the sediment surface.

R<sub>a</sub> and R<sub>g</sub> can be written

$$R_{a1} = \ln (b_1 2^{(-m/h)} / k_1) / -i \quad (2)$$

$$R_{g1} = \ln (cd_1 2^{(-g/h)} / k_1) / -i \quad (3)$$

where

- b = amount of autochthonous carbon in percent;
- c = constant, proportional to the influence of the penguin proxy;
- d = penguin proxy;
- g = apparent age of the guano;
- h = half-life of <sup>14</sup>C, 5568 yr;
- i = proportionality constant,  $i = \ln 2/h$ ;
- k = amount of carbon in the sample in percent;
- m = apparent age of the autochthonous carbon in years.

The amount of autochthonous carbon (b) can be written

$$b_1 = k_1 - cd_1 - ef_1 \quad (4)$$

where

- e = constant, proportional to the influence of particulate bedrock/soil carbon.
- f = amount of minerogenic material in the sample in percent.

Equations (1), (2), (3) and (4) can be combined to produce the expression:

$$a_1 = j_1 - (\ln(((k_1 - cd_1 - ef_1)2^{(-m/h)} + cd_1 2^{(-g/h)})/k_1)/-i). \quad (5)$$

Equation (5) demonstrates how the “true”  $^{14}\text{C}$  age of a sample can be calculated and will be applied to each of the six dated samples. This leaves 6 simultaneous equations, 1 for each sample, and 10 unknowns: the constants,  $c$  and  $e$ ;  $j_{1-6}$ , the “true”  $^{14}\text{C}$  ages of samples 1 to 6; and  $g$  and  $m$ , the apparent ages of the penguin guano and autochthonous carbon, respectively. Of the unknowns,  $c$ ,  $e$ ,  $g$  and  $m$  are identical for all samples. These simultaneous equations are called the  $^{14}\text{C}$  model. Some unknowns in this model must be estimated or assigned a reasonable value (discussed later), so that, at most, six unknowns remain and the simultaneous equations can be solved.

I ran the model several times (*i.e.*, the six simultaneous equations were solved) and the values of the unknowns changed from their previous values between the runs. The new value assigned to the unknown depended on the outcome of previous model runs and reasonable assumptions. I ran the model until the “true”  $^{14}\text{C}$  ages  $j_{1-6}$  were compatible with both the lithostratigraphy of the sediment and a reasonable sedimentation rate. At the same time, I used reasonable values for the influence of carbon from different sources,  $c$  and  $e$ , and the apparent ages of this carbon,  $g$  and  $m$ .

## RESULTS AND DISCUSSION

Lake Boeckella sediments are enriched in six elements—Ca, Cd, Cu, P, Sr and Zn—compared to the mean concentrations of the elements in the reference lake deposits (Figs. 2A–F). One of the 16 samples from the sediment core of Lake Boeckella was excluded from further analysis because of an exceptional chemical composition that makes the sample unrepresentative for the core as a whole. Two penguin guano samples were outliers, and were excluded from further analyses. Because the rookeries were completely abandoned at the time of sampling, it is possible that some samples represent old, partly decomposed guano.

The chemical analyses demonstrate that Ca is the only 1 of the 6 elements showing a significantly higher concentration when the sample is melted with  $\text{LiBO}_3$  rather than leached with  $\text{HNO}_3$ . This shows that none of the enriched elements, except Ca, is bound to primary minerals, and that the bedrock is not the major source of these elements.

Lake Boeckella is eutrophic because it receives nutrients from the Adélie penguin rookery on the lake shores (Izaguirre *et al.* 1993), as is evident, for example, from the fact that all of the measured elements except Fe and Ba are present in higher concentration in the outlet than the inlet water. This indicates that the major source of these substances is not as solubles in the inflowing meltwater.

It seems reasonable to compare results from leached sediment samples with results from penguin guano. Both routines partly dissolve the sample, but leave most of the primary minerals undissolved. The comparison shows that the concentrations of the enriched elements in the upper four samples from the core approach or reach the mean concentrations of these elements in the guano (Figs. 2A–F). This is another indication that the guano is the major source of these elements and that the upper part of the core consists mainly of guano.

LOI correlates fairly well with the six enriched elements in the sediment of Lake Boeckella (Pearson correlation matrix,  $r$  0.72–0.88). Carbon from the penguin guano washes into the lake, but in addition, P in the guano acts as a fertilizer and stimulates autochthonous production, thereby raising the concentration of carbon in the sediment.

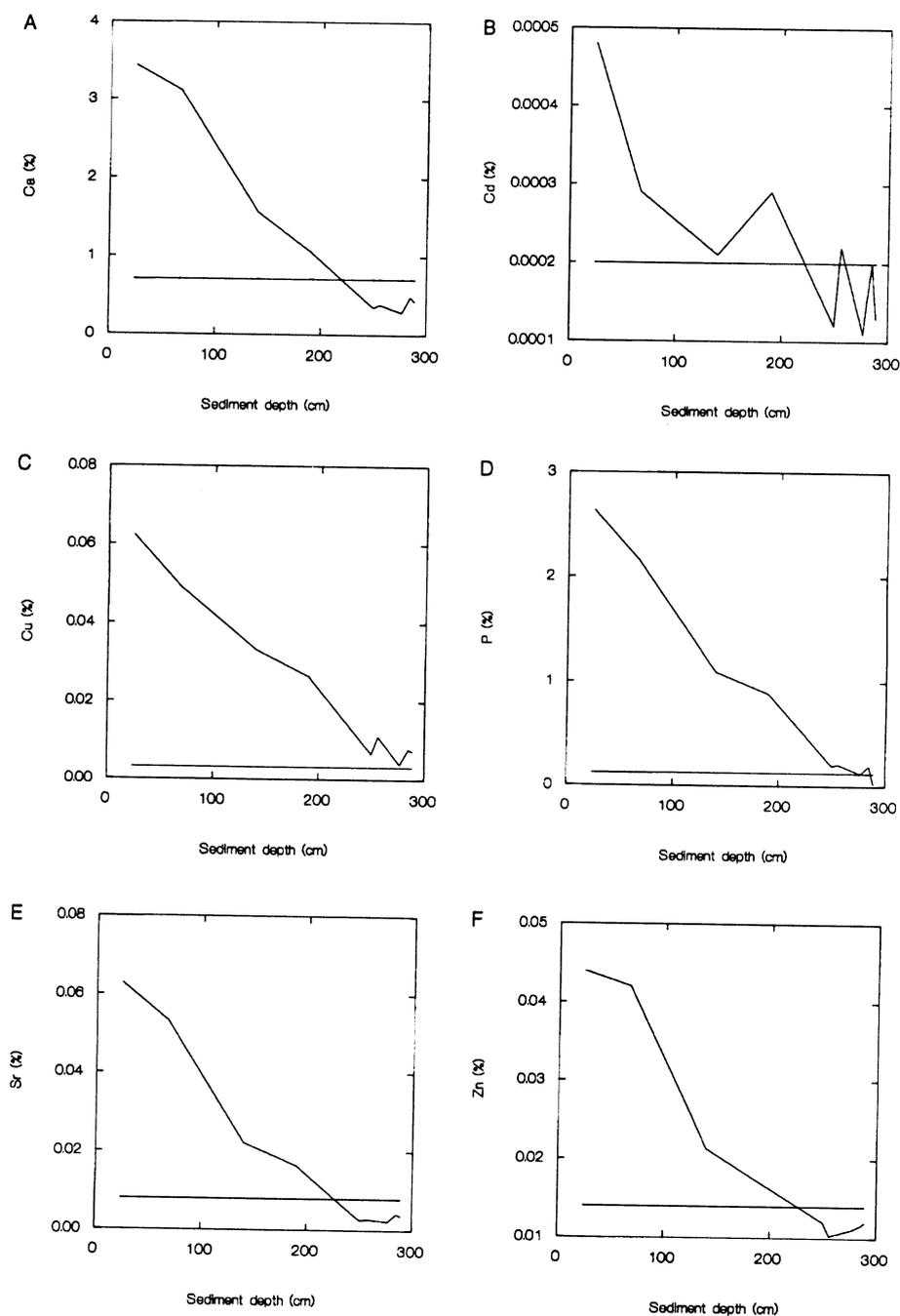


Fig. 2 A-F. Concentrations of Ca, Cd, Cu, P, Sr and Zn from leached samples vs. sediment depth in Lake Boeckella. Samples were analyzed from the following sediment depths (cm): 22-25, 41-45, 61-62, 66-67, 99-101, 139-140, 143-144, 187-188, 189-190, 249-251, 255-256, 265-270, 276-277, 284-286, 288-290. The mean concentrations of the same elements in the sediments from the reference lakes are shown as straight lines. Mean and  $1\sigma$  concentrations of the elements in the penguin guano were:  $6.6 \pm 1.9\%$  Ca;  $0.00024 \pm 0.00014\%$  Cd;  $0.042 \pm 0.023\%$  Cu;  $4.8 \pm 1.3\%$  P;  $0.012 \pm 0.006\%$  Sr; and  $0.044 \pm 0.030\%$  Zn.

### Elements Suitable as a Penguin Proxy

Phosphorus and most heavy metals are stable in sediment under most circumstances and are thus suitable as proxies (Dearing 1986). However, determining which elements in Lake Boeckella sediment are stable and which are not is difficult, because only a few chemical analyses were performed and similar lakes have seldom been investigated. The good correlations between Ca, Cd, Cu, P, Sr and Zn (Pearson correlation matrix) in the sediment indicate either that these elements are stable or that their mobility in the sediment is similar.

The concentrations of an element in the sediment samples used to calculate the background level must be normally distributed; otherwise, a significance level cannot be set. A variety of the Kolmogorov-Smirnov test, the Lilliefors test, shows that only the concentrations of Ca, Cu and P in the samples from the reference lakes are normally distributed (level of significance 95%). This means that the selection of reference lakes and/or sampling depths was biased w.r.t. the concentrations of Cd, Sr and Zn. Thus, the background concentrations of these elements cannot be used in further statistical analyses. In addition, concentrations of the selected elements should not be significantly lower in the study-lake sediments than the background levels measured in reference lakes. This criterion rules out Ca. Therefore, only Cu and P were used to evaluate the impact of guano on the sediment.

It seems reasonable to use the following as a proxy (unitless) for the penguin impact on the sediment

$$\text{Proxy} = (((A_P - U_P)/B_P) + ((A_{Cu} - U_{Cu})/B_{Cu}))/2 \quad (6)$$

where

- A = concentration in Lake Boeckella;
- U = upper confidence limit of the background level;
- B = mean background level.

Subscripts denote the element in question. Zero or a negative value means that no penguin effect can be detected in the lake sediments.

### The <sup>14</sup>C Dating Model

#### *The Apparent Age of the Penguin Guano*

The apparent age of penguin guano is probably close to the apparent age of the penguins. Björck *et al.* (1991) reported a pre-bomb (1903) penguin collagen date from Hope Bay of  $1280 \pm 50$  BP. The date gives a reservoir effect of 1230 yr for Adélie collagen from this area, a reasonable starting value for the apparent age of the penguin guano (g) in the model used here, since no published guano dates from the area were found. An "industrial effect" correction would be, at most, 20 yr and is thus negligible. Stuiver and Braziunas (1985) made an extensive compilation of Antarctic isotopic dates.

#### *The "True" <sup>14</sup>C Ages of the Topmost Samples*

If the "true" <sup>14</sup>C ages of the two topmost samples are set to reasonable values considering the sedimentation rate, and the apparent age of the autochthonous carbon (m) is set to 0, then two simultaneous equations (2 forms of Equation (5)) with 2 unknowns, the proportionality constants c and e, can be solved, and the values of c and e can be determined. The values of c and e can then be used to calculate the "true" <sup>14</sup>C ages of the other samples, and the result checked by comparing the sedimentation rates in different parts of the core.

The "true"  $^{14}\text{C}$  age of sample 1 (1-cm depth) is somewhat difficult to determine. The upper sediment might be contaminated with bomb  $^{14}\text{C}$ , producing a supermodern date (*cf.* Druffel 1981; Mabin 1986; Whitehouse *et al.* 1987). However, penguins, and thus fresh penguin guano, do not seem to be contaminated with bomb  $^{14}\text{C}$  because ages of freshly killed Adélie penguins (Omoto 1983) are in reasonable agreement with ages of Adélie's killed before 1950 (Whitehouse *et al.* 1987). Poisson and Chen (1987) reported a deficiency of anthropogenic  $\text{CO}_2$  in the Weddell Sea, which might explain why penguins are not affected by bomb  $^{14}\text{C}$ . Because sedimentary carbon largely originates from penguin guano (the penguin proxy = 5.1 in sample 1), a "true"  $^{14}\text{C}$  age of sample 1 is probably close to -37 BP (AD 1987 subtracted from AD 1950).

The "true"  $^{14}\text{C}$  age of sample 2 (12-cm depth) must be based on sedimentation rates. It is reasonable to assume that the apparent linear sedimentation rate diminishes because of sediment compaction. If the "true"  $^{14}\text{C}$  age of sample 2 is set at 3 BP, then the apparent sedimentation rate between samples 1 and 2 is 3.0 mm  $\text{yr}^{-1}$ .

The proportionality constants, *c* and *e*, can be determined by solving two simultaneous equations (Eq. (5)) for the two topmost samples with sample 1 set at -37 BP and sample 2 at 3 BP. The result (Table 1, top) suggests a reasonable sedimentation rate between sample 2 and sample 3 (99-cm depth and 460 BP) of 1.9 mm  $\text{yr}^{-1}$ . These values are open to discussion, but the "true"  $^{14}\text{C}$  ages of samples 1 and 2 are not at all critical, as can be seen from Table 1 (bottom). The shaded area encloses the ages

TABLE 1. The dated bulk sediment samples (top half of the table) and the dates calculated by the model for samples 3-6 (bottom half) depending on the ages chosen for samples 1 and 2 (bottom half). The values of *cd* (amount of carbon from penguin guano, bottom half, columns 1-3) depend on the ages chosen for samples 1 and 2 and the apparent age of the penguin guano. Shaded area represents the dates calculated by the model with sample 1 set to -37 and sample 2 to 3 BP,  $\pm 1 \sigma$  of the original date.

Sample no.	1	2	3	4	5	6
Sediment depth (cm)	1	12	99	159	219	279
Carbon content (%)	8.1	13.0	20.3	16.5	13.4	5.5
Minerogenic content (%)	86	78	63	72	79	92
Penguin proxy	5.1	16.6	20.9	5.9	7.0	0.6
Lab no. (St-)	11990	11746	11747	11620	11748	11619
$\delta^{13}\text{C}$ (‰)	-28.0	-28.4	-27.0	-22.8	-25.7	-25.4
$^{14}\text{C}$ age BP	2275	2585	2140	3720	4085	8615
Age $\pm 1 \sigma$	70	70	70	70	120	170

Values of $\text{cd}_2$ (%) if $g=1000 \text{ yr}$	Values of $\text{cd}_2$ (%) if $g=1230 \text{ yr}$	Values of $\text{cd}_2$ (%) if $g=1500 \text{ yr}$	Ages of samples 1 and 2 used as input		Ages for samples 3-6 as calculated by the model			
			1	2	3	4	5	6
16.8	13.9	11.6	-137	13	492	2588	2468	5101
18.3	15.1	12.6	- 37	- 27	436	2618	2507	5412
18.2	15.0	12.5	- 37	- 17	444	2619	2509	5402
18.0	14.9	12.4	- 37	- 7	452	2619	2511	5392
17.9	14.7	12.3	- 37	3	460	2620	2512	5381
17.7	14.6	12.2	- 37	13	468	2621	2514	5371
17.6	14.5	12.1	- 37	23	477	2622	2516	5360
17.4	14.3	11.9	- 37	38	489	2624	2518	5345
17.0	14.0	11.7	- 37	63	509	2626	2522	5318
16.3	13.5	11.2	- 37	113	551	2630	2531	5265
15.6	12.9	10.7	- 37	163	592	2635	2539	5112
15.8	13.3	10.9	63	213	610	2673	2593	5428

for samples 3–6,  $\pm$  the counting error of the original date (*i.e.*,  $1\sigma$  as reported for the sample age from the laboratory) calculated when sample 1 is set to  $-37$  BP and sample 2 to 3 BP. Thus, a reasonable “true”  $^{14}\text{C}$  age for sample 1 is  $-37$  BP, and 3 BP for sample 2.

#### *The Proportion of Allochthonous vs. Autochthonous Carbon and the Apparent Age of the Penguin Guano*

The results of the modeling can be checked by the products, cd and ef, as these give the amount of carbon originating from the penguin guano and the watershed bedrock/soil, respectively (the apparent age of the autochthonous carbon, m, is still 0). The critical sample in the core is sample 2, where the penguin proxy is high and the amount of carbon, low. The amount of carbon from the bedrock/soil in the chosen example (“true”  $^{14}\text{C}$  ages of  $-37$  BP for sample 1, and 3 BP for sample 2) is calculated by the model (ef) to be 1.5% in sample 2. This leaves room for a maximum contribution from the penguin guano of 11.5% (as the amount of carbon in the sample is 13.0%), which is lower than calculated by the model, as shown in Table 1. The amount diminishes when the difference in age between sample 1 and 2 and/or the apparent age of the penguin guano increases.

If the amount of carbon originating from the bedrock/soil and the penguin guano is set at 13%, *i.e.*, the primary source in the lake was “old” carbon ( $b=0$ ), then the apparent age of the penguin guano is calculated to 1610 yr, which is not unreasonable. Omoto (1983) concluded that the reservoir effect in Antarctica ranges between 0.8 and 3 ka. On the other hand, if the amount of carbon originating from the bedrock/soil and the penguin guano is set to 13%, and the apparent age of the penguin guano is set to 1230 yr, the model calculates the “true”  $^{14}\text{C}$  age of sample 2 as 370 BP and sample 3 as 793 BP. This gives an apparent linear sedimentation rate between sample 1 and 2 of  $0.29\text{ mm yr}^{-1}$  and between sample 2 and 3 of  $2.1\text{ mm yr}^{-1}$ . I consider these figures highly unlikely, especially as no dramatic change in the sediment was found in this part of the core (Zale and Karlén 1989). Thus, a large portion of the sediment carbon stems from the penguin guano, the apparent age of which is at least 1610 yr.

#### *The Influence and Apparent Age of the Autochthonous Carbon*

If the apparent age of the autochthonous carbon (m) is set to positive values smaller than the apparent age of the penguin guano, then c (proportionality constant) increases. This requires that the apparent age of the penguin guano (g) is even older than 1610 yr. For example, if sample 1 is set to  $-37$  BP, sample 2 to 3 BP, and the apparent age of the autochthonous carbon (m) is set to 0.5 ka, the apparent age of the penguin guano (g) is calculated by the model to 1829 yr. The age of sample 3 is calculated to 256 yr, and the ages of the rest of the samples differ in this example *ca.* 250 yr from the calculation where the apparent age of the autochthonous carbon (m) is set to 0 BP. This gives sedimentation rates between sample 1 and 2 of  $0.37\text{ mm yr}^{-1}$  and between 2 and 3 of  $3.4\text{ mm yr}^{-1}$ . The core provides no evidence of such a large change in sedimentation rate.

Apparent ages of the autochthonous carbon older than the apparent age of the penguin guano give unacceptable, supermodern results. A negative apparent age for the autochthonous carbon (m) is also highly unlikely. Thus, the apparent age of the autochthonous carbon is small, and its influence on the dates is negligible. This means that no effect of “old” glacial meltwater or dissolved bedrock carbonates can be detected. The chemical analyses support the view that the “hard water effect” resulting from carbonates in the bedrock is of minor importance, as evident from the anomalously low Ca content (Fig. 2A) in the lowermost sediment, which is not affected by penguins.

### The Influence of the Allochthonous Carbon

Suppose the “true”  $^{14}\text{C}$  age of sample 1 is set to  $-37$  BP, sample 2 to 3 BP, the influence from the carbon originating from the penguin guano (c) to 0 and the apparent age of the autochthonous carbon (m) to 0. If the influence of the carbon from the bedrock/soil (e) is calculated, the result will also be unacceptable, *i.e.*, the error in the calculated date is  $>2$  ka. Thus, “old” carbon originating from the penguin guano influences the  $^{14}\text{C}$ -dating of the sediment.

Suppose the “true”  $^{14}\text{C}$  age of sample 1 is set to  $-37$  BP, sample 2 to 3 BP, and the influence of “old” carbon from the watershed bedrock/soil (e) is set to 0. The apparent age of the autochthonous carbon (m) and the influence of carbon from the penguin guano (c) can then be calculated. This results in errors of  $\sim 0.5$  ka for sample 2, or unacceptable negative or very large values. Thus, “old” carbon from the bedrock/soil also influences the  $^{14}\text{C}$  ages.

### The $^{14}\text{C}$ Ages

One of the calculated ages for samples 4 (159-cm depth) and 5 (219-cm depth) must be erroneous as sample 4 cannot be older than sample 5. The validity of sample 4 was discussed previously (Zale and Karlén 1989). If the calculated date of sample 4 is accurate, but not that of sample 5, the resulting curve of sedimentation rates indicates changes for which no evidence exists in the core (Fig. 3). Based on this and the fact that sample 4 has the highest  $\delta^{13}\text{C}$  value of all, indicating a possibly different origin of the carbon used for dating (Table 1), I believe that the dating of sample 5 is more likely to be correct than that of sample 4.

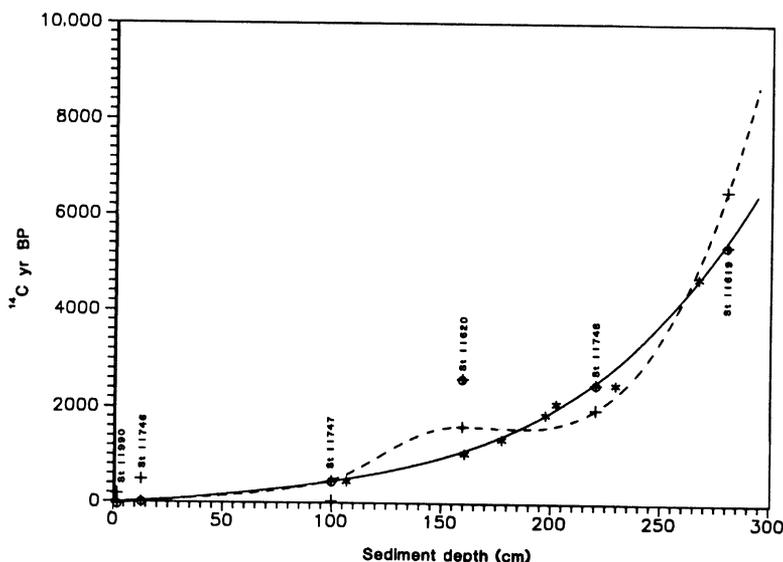


Fig. 3. Sediment depth vs.  $^{14}\text{C}$  age in Lake Boeckella. - - - from Zale and Karlén (1989), based on  $^{14}\text{C}$  ages (+) minus a constant reservoir effect. — is based on the tephrochronology of Björck, Sandgren and Zale (1991). \* = tephra horizon. ⊕ = ages calculated from the  $^{14}\text{C}$  model.

### The $\delta^{13}\text{C}$ Values

The  $\delta^{13}\text{C}$  values of the samples (Table 1) agree with the *ca.*  $-22\text{‰}$   $\delta^{13}\text{C}$  values for Adélie guano (Hebert 1980), and the  $-22$  to  $-25\text{‰}$  for penguin remains (Whitehouse *et al.* 1987, Björck *et al.* 1991). These values are not surprising because krill, the main diet of Adélies, has  $\delta^{13}\text{C}$  values of *ca.*  $-28\text{‰}$  (Wand 1987).

### The Model

Björck, Sandgren and Zale (1991) studied the late Holocene tephrochronology of the northern Antarctic Peninsula. They found seven tephra horizons in Lake Boeckella by chemical and magnetic analyses, which they correlated to  $^{14}\text{C}$ -dated tephra horizons in sediments from other locations around the Antarctic Peninsula. A comparison between the sediment depth vs. age curve (Fig. 3) and the independently dated tephra clearly demonstrates that the ages as calculated with the  $^{14}\text{C}$  model are more accurate than the ages reported by Zale and Karlén (1989). The date, St-11620,  $3720 \pm 70$  BP (Table 1), is clearly erroneous, as suggested earlier by Zale and Karlén (1989).

The model can also be used to draw the penguin proxy as a function of time (Fig. 4). Penguins have occupied the lake shores since *ca.* 5550 BP, except for a brief discontinuity *ca.* 5200 BP. This is in line with both Birkenmajer (1981), who dated penguin remains to 4950 BP, and Barsch and Mäusbacher (1986), who dated penguin bones from King George Island to *ca.* 5300–5800 BP. The penguin influence reached a maximum at *ca.* 40 BP and has since declined drastically. The size of the rookery is probably climate-dependent.

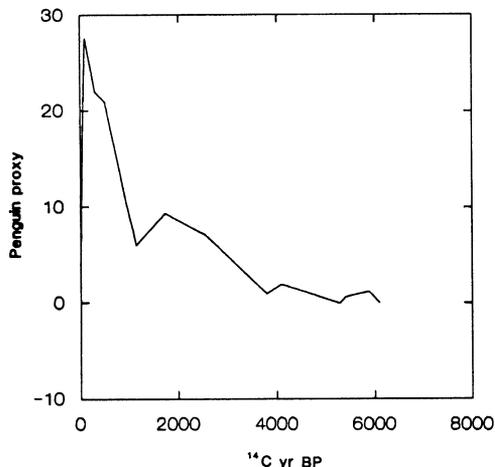


Fig. 4. The proxy for the penguin influence on the lake sediment vs.  $^{14}\text{C}$  age. Ages calculated by the model were used. The plot uses the 9 samples chemically analyzed and the 6 samples both chemically analyzed and dated.

If the modeling results are used to recalculate the result of Zale and Karlén (1989), most of the changes are small. The major change is that the deglaciation occurred *ca.* 6300 BP instead of 8680 BP as previously thought, and the climatic deterioration culminates *ca.* 4700 BP instead of 5000 BP. The model also suggests that the reservoir effect has been constant for *ca.* 5800  $^{14}\text{C}$  yr in this area. This implies long-term stability of the currents and water masses around the tip of the Peninsula.

### CONCLUSIONS

I have developed a  $^{14}\text{C}$  dating model to show that the  $^{14}\text{C}$  age correction factor in Lake Boeckella depends mainly on the amount of penguin guano in the lake sediment, the apparent age of the guano and the amount of carbon originating from the soil/bedrock. The model also shows the apparent age of the penguin guano to be at least 1610 yr. The supposedly "old" glacial meltwater does not affect the correction factor, nor do dissolved carbonates from the watershed bedrock/soil, *i.e.*, I can find no hard water effect. The model suggests that the reservoir effect has been constant for the last 5800  $^{14}\text{C}$  yr, implying a long-term stability of the water masses and currents in the area.

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