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Late Holocene records of Antarctic Fur Seal (*Arctocephalus gazella*) population  
variation on South Georgia, sub Antarctic

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MSc by Research

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2005

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Late Holocene records of Antarctic Fur Seal (*Arctocephalus gazella*) population variation on South Georgia, sub Antarctic.

Foster, V. A (2005)

The Antarctic fur seal (*Arctocephalus gazella*) population at South Georgia has increased dramatically through the 20<sup>th</sup> and 21<sup>st</sup> centuries following near extinction at the beginning of the 20<sup>th</sup> century. This rapid increase is now causing concern as the seals are damaging the coastal habitats of South Georgia including specially protected areas. To assess whether this population increase is part of a natural fluctuation or due to human induced changes in the marine ecosystem, the fur seal population has been reconstructed through the Holocene from seal hair abundance and geochemistry. Results from the fur seal hair abundance record show fur seals have been present at South Georgia for at least the past 3439 <sup>14</sup>C yrs BP and the population today is not unprecedented during the late Holocene. Although previous studies have found a correlation between fur seal populations and geochemistry, this study highlights that this is not effective at all study sites due to the complex relationship between climate change, catchment sediment delivery processes and seal population dynamics. At South Georgia, Cu and Zn are found to be indicators of fur seal activity once a threshold of 1500 hairs per 1 g of dry weight is reached.

The fur seal hair abundance results suggest there is a link between fur seal populations and climate change. Although the largest increases in fur seal population occur during cooler periods, the fur seal population is primarily controlled by prey availability (*Euphausia superba*), which is in turn influenced by climate change. Pre 200 yrs BP, an increase in prey availability is associated with colder periods, which are linked to changes in oceanography and led to a consequent increase in sea-ice extent. Post 200 yrs BP, the whaling industry has resulted in a krill surplus in the South Georgia region elevating krill availability, causing an increase in the fur seal population (that has been coincident with warming). Although the population has increased during the 20<sup>th</sup> and 21<sup>st</sup> century as a result of human induced causes, this increase cannot be sustained once the krill surplus ceases. As the population has been at similar levels previously and the krill surplus is thought to be ending, it is concluded that the fur seal population increase during the 20<sup>th</sup> century is not abnormal and management of the fur seal population at South Georgia may not be necessary.

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## Declaration

I certify that this thesis is the result of my own work and has not been submitted for any other examination. Material from the published or unpublished work of others, which is referred to in the thesis is credited to the author(s) in question in the text.

## Statement of copyright

The copyright of this thesis rests with the author. No quotation from it should be published without their prior written consent and information derived from it should be acknowledged.

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# Chapter 1

## Introduction and Aim



Plate 1: Fur seal (*Arctocephalus gazella*)

## 1 Introduction and Aim

### 1.1 Research Context

It is widely recognised that Antarctic fur seal (*Arctocephalus gazella*) populations on the Antarctic Peninsula and surrounding Sub-Antarctic islands have rapidly increased in the past few decades (Hodgson *et al.* 1998; Payne 1977). However, during the early 20<sup>th</sup> century fur seals were almost extinct following human exploitation during the 19<sup>th</sup> century (Bonner 1968). It is estimated that by 1825, 1,200,000 fur seal skins had been taken from the sub-Antarctic region (Headland 1982). The most rapid population increase has occurred on the island of South Georgia, where the fur seal population was almost 3,000,000 in 1999 (ATCM 1999). Such a fast increase in fur seals is now causing extensive changes to terrestrial and freshwater systems and in some areas damaging Antarctic Specially Protected Areas (ASPAs) (Hodgson *et al.* 1998; Lewis-Smith 1988). If the fur seal population continues to grow at the same rate, it is possible that the fur seal impact is likely to have a catastrophic and irreversible effect on the Antarctic ecosystem; however, it is not yet clear if the increase in fur seal populations is due to climate change, recovery from exploitation or other natural variations.

With respect to climate change there is a broad scientific consensus that the warming of the earth's climate since the 1970s is greater than any time in the last thousand years (IPCC 2001). This has caused concern regarding the biological and ecological changes affecting the range and distribution of species (Croxall *et al.* 2002). The key to determining the impact of climate on the Antarctic ecosystem (and specifically fur seals) is to determine the range of natural variability in the ecosystem and to distinguish natural changes from human perturbations (Abbott and Benninghoff 1990).

To overcome the problems distinguishing between the human impact and the impact of natural environmental change on fur seal populations, Hodgson and Johnston (1997) used palaeolimnology to reconstruct fur seal populations going back several centuries/millennia, prior to human intervention. This study is based upon the theory that fur seals moult regularly, depositing hair in terrestrial and aquatic environments. This hair is

washed into lakes and incorporated into the lake sediments hence, providing a proxy record of fur seal presence.

## 1.2 Overall Aim

The aim of this study is to reconstruct the fur seal population of South Georgia by counting seal hairs from a South Georgia lake sequence as a proxy for fur seal abundance combined with geochemical analysis using techniques outlined by Hodgson *et al.* (1998) and Sun *et al.* (2004a). Comparing the fur seal population fluctuations during the 20<sup>th</sup> century and the late Holocene will allow the controlling factors underlying these population fluctuations to be better understood and hence, aid management and conservation decisions. Within this central aim lie a number of specific objectives which are outlined below.

## 1.3 Specific Objectives

1. To reconstruct fur seal populations through the late Holocene by counting seal hairs from a lake on South Georgia.

This objective seeks to assess the changes in fur seal population, prior to, during and since exploitation. As highlighted by Ellis-Evans (1990), long-term monitoring studies are needed to determine the direction and rate of environmental and ecological change, assessing the resilience of ecosystems to and their recovery from these phenomena. Counting seal hairs in a lake sediment sequence provides a proxy for fur seal populations through the late Holocene and hence, allows the reconstruction of a continuous record of fur seal populations both prior to and during human intervention. Comparing this record with other data on environmental and ecological changes will allow an assessment of the link between the ecosystem and environmental change.

2. To reconstruct fur seal populations indirectly using geochemical analysis, following the method outlined by Sun *et al.* (2004a).

By analysing a range of geochemical proxies it will be possible to not only provide an additional proxy for the fur seal populations and help to validate the method outlined by

Hodgson *et al.* (1998), but it will also provide proxy (ies) for climate change at the site and hence, allow comparison of the fur seal population and climatic change.

3. To determine whether recent (20<sup>th</sup> –21<sup>st</sup> century) increases in fur seals have exceeded the range of natural variability of past populations.

As Croxall (1992) indicates, all documented population changes of fur seals relate to human exploitation. Using fur seal hair abundance and geochemical analysis as a proxy for fur seal populations during the Holocene allows a record of fur seal populations prior to the 20<sup>th</sup> century to be constructed, thereby allowing the magnitude of the 20<sup>th</sup> – 21<sup>st</sup> century changes in relation to changes prior to human intervention to be assessed. The record of fur seal populations prior to human intervention will help to determine both the range of natural variability in the Antarctic ecosystem and the magnitude of human perturbations (Abbott and Benninghoff 1990).

4. To review and assess the impact that environmental changes on South Georgia have had upon seal populations over the Late Holocene.

Using a combination of published and instrumental climate data through the 20<sup>th</sup> century and published proxy data through the late Holocene, this record will provide a means of determining the environmental changes at South Georgia. This record will be correlated with the reconstructed fur seal population data to help to determine the impact environmental changes have had upon fur seal population changes.

5. To determine the factors controlling fur seal population changes at South Georgia through the late Holocene.

Reconstructing population changes through the late Holocene allows an assessment of factors controlling the population variations prior to human intervention. Comparing these changes with 20<sup>th</sup> century variations, the impact of human intervention on the fur seal population can be assessed. This is essential to determine the appropriate management measures required to control the population explosion.

## 1.4 Mechanisms influencing fur seal populations

As discussed in section 1.1, there are two broad mechanisms for fur seal population growth; natural environmental changes and human induced changes. As human induced changes correlate with the fur seal population data, to distinguish between these two mechanisms there is a need to reconstruct the fur seal population through the Late Holocene. To provide a context for the aims and objectives, these possible mechanisms for fur seal population growth are considered briefly, before being discussed in further detail in chapter 2.

### 1.4.1 Natural environmental changes

Natural environmental changes such as deglaciation and global warming alter the environment and its ecosystems. It is possible that natural changes in the environment could now be more favourable for fur seal survival than the early 20<sup>th</sup> century when populations were significantly lower than today. However, this timing also corresponds to human intervention and so the impact of natural environmental changes may be obscured. As Lewis-Smith (1990) indicates, the present climate warming is central to local changes in terrestrial and marine ecosystems, directly and indirectly influencing biological processes. For example, Laws (1977) suggests that climate warming may produce fluctuations in food availability, which may indirectly affect changes in predator populations such as fur seals. Other changes occur as a function of the natural process of ecosystem development, strongly influenced by minor variations in climate or other components of the environment. For example, as Croxall (1992) documents, changes in krill populations correlate with major ENSO events. The magnitude and persistence of these changes cannot be explained by natural variations in krill demography and hence, must involve large-scale distribution changes influenced by ocean- atmospheric processes. This variation in fur seal food supply may directly affect the population changes. For example, on Possession Island, Guinet *et al.* (1994) document significant decline in fur seal pup production the year after ENSO events.

To determine whether an effect can be detected on the Southern Ocean scale, there is a need to examine long term data on demographic parameters obtained for seabirds and marine mammals for different breeding localities where long term monitoring programmes are conducted. This has been done on King George Island, where Sun *et al.*

(2004a) provide a 1500-year record of seal populations and highlight that before human influence, fur seal populations exhibited dramatic fluctuations. Comparing this record with paleoclimatic data suggests that increases in seal populations roughly corresponded to warm periods and decreases in population correlated with cooler periods, suggesting that natural environmental changes, such as sea ice cover and atmospheric temperature have historically had a large impact on seal populations. As King George Island is located to the south of South Georgia and experiences different climate conditions, the ecosystem is under different pressures than South Georgia, thus, it cannot be assumed that this correlation between fur seal populations and climate will also occur at South Georgia.

#### 1.4.2 Human induced changes

Hodgson *et al.*'s (1998) study of Signy Island suggests there is a lack of correlation between fur seal populations and climate during the late Holocene. This is in contrast to Sun *et al.* (2004a) and Guinet *et al.* (1994) that state that populations have been a similar magnitude during the late Holocene as seen today. Hodgson *et al.* (1998) suggest there is a distinct correlation between a rapid decrease in fur seal populations and human intervention, suggesting that human intervention is the causal mechanism for the recent 20<sup>th</sup>–21<sup>st</sup> century changes. Evidence indicates that fur seal populations at Signy Island are now greater than pre-exploitation levels, implying that factors that were not present prior to exploitation have affected the population growth (Hodgson *et al.* 1998). As human intervention was limited before exploitation, it is thought that human interactions with environment are sufficient to alter the population. One of the prime influences on the fur seal population of South Georgia has been the sealing and whaling industries during the 18<sup>th</sup>, 19<sup>th</sup> and 20<sup>th</sup> centuries, which have been discussed in the following terms.

##### 1.4.2.1 Sealing

Sealing at South Georgia developed rapidly in the latter part of the 18<sup>th</sup> and early 19<sup>th</sup> centuries (Headland 1982). Activities peaked around 1800, after this time the seal stocks were so depleted that sealers began to exploit other islands, such as the South Shetland Islands although the sealing on South Georgia continued at very low levels. In 1925, it was estimated that a total of 1,200,000 fur seal skins had been taken from South

Georgia during the sealing period and the quantity of elephant seal oil extracted was 20,000 tons (Bonner 1968). During the beginning of the 20<sup>th</sup> century the fur seal population at South Georgia was near extinction and it was not until the 1930's the first fur seal pups were recorded at South Georgia (Boyd 1993).

#### 1.4.2.2 Whaling

South Georgia was the principal centre for whaling in the Southern Hemisphere from its establishment in 1906 to 1966 when stocks depleted, although restrictions had been enforced from 1906 to prevent over-exploitation (Headland 1982). The prime impact of the whaling industry on the fur seal is thought to be the increase in abundance of krill. Whales feed primarily on krill; therefore a reduction in the number of whales caused a krill surplus (Croxall 1992). This increase in krill allowed a greater fur seal population to be supported and led to an increase in fur seals. It is this krill surplus that is now widely recognised as the most probable cause of the recent increase in fur seals (Doidge and Croxall 1985; Croxall and Prince 1979; Croxall 1992; Green et al. 1989).

#### 1.5 Summary

This dissertation is structured in the following way in order to address the aim and objectives outlined above. Chapter two builds upon this background and outlines the rationale for the aims and objectives discussed above. Following this, chapter 3 outlines the methodology I used to produce the results, which are presented in chapter 4. Chapter 5 discusses the results and the implications these results have on my objectives. I shall then briefly conclude the study by readdressing the overall aim in chapter 6 and then assessing the study's limitations and potential for future work in chapter 7.

## Chapter 2

### Background and Rationale



Plate 2: Maiviken bay

## 2: Background and Rationale

This chapter outlines the background on which this study is based. Firstly I outline the study site and the reasoning for choosing South Georgia. This is followed by a discussion of the climate changes from proxy records through the late Holocene to use when answering objective 4. The chapter ends on an evaluation of the size and growth of the fur seal population in the 20<sup>th</sup> century, the possible causes for this population growth and the impacts of this population growth.

### 2.1 Rationale for study location

The study uses two sediment cores from Maiviken, South Georgia, primarily because today 95% of the world's fur seal population breeds at South Georgia and secondly, as South Georgia has experienced the most rapid increase in 20<sup>th</sup> century fur seal population growth throughout the Antarctic region (Croxall 1992). Such an increase in the fur seal population at South Georgia has resulted in the collection of extensive fur seal population census data and detailed research on the population structure and development (Bonner 1968; Croxall and Prince 1979; Laws 1973; Payne 1977). This record provides an important historical fur seal population record, against which the proxy evidence derived using palaeolimnology can be compared (Laws 1973). In addition to these factors, extensive research has been carried out on the biological interactions of the fur seal at South Georgia. For example, Doidge and Croxall (1985) provide evidence for the diet and energy budget of the fur seal at South Georgia, whilst North *et al.* (1983) and Barlow *et al.* (2002) both established the primary fur seal prey and competition. This additional biological research provides a good basis to understand fur seal interactions with the environment hence, aiding further analysis.

It is widely implied that the human induced causes for the recent change in fur seal populations are the sealing and whaling industries (Croxall 1992). As these activities were generally more widespread and intensive on South Georgia, than elsewhere in the sub Antarctic region, the impact of these activities are more easily identified. Natural causes of the population increase are primarily thought to be climatic change (Sun *et al.* 2004a). As Rosqvist *et al.* (1999) indicate, South Georgia is situated in a prime location to study climatic connections between temperate and polar environments in the Southern Hemisphere. For this reason, extensive climate reconstruction has occurred

around South Georgia allowing comparisons between fur seal population fluctuations and climate changes to be evaluated. In addition to this, South Georgia is located on the boundary of the temperate and polar environments therefore, it experiences large climate fluctuations and as a consequence it is likely that the fur seal population here will respond more rapidly to these changes than in other areas of the Southern Ocean (Rosqvist *et al.* 1999).

### 2.2 Study Site

#### 2.2.1 South Georgia

South Georgia is an isolated island in the Southern Ocean, located at 54° S and 34° W (see figure 2.1). The island is approximately 170 km long and ranges from 2 to 30 km wide (Headland 1984). Surrounding the island are several smaller islands, the major one being Bird Island off the western extremity (see figure 2.1.1).

The principal mountain chain of the island is the Allardyce Range, with the highest peaks located towards the centre of the island, thus, providing a barrier against the severe weather that reaches the south west of the island (Headland 1984). The climate is governed by the island's position relative to the polar frontal zone and related westerlies. Due to this location the climate today is cold, wet and cloudy but with no great seasonal variation (*ibid*). Mean temperature is 1.8°C and mean precipitation is 1393 mm per year (Rosqvist *et al.* 1999). Today the polar front is approximately 250km north of South Georgia in the eastward flowing Antarctic Circumpolar Current (ACC) (Atkinson *et al.* 2001). To the west of South Georgia, the Scotia ridge deflects the ACC northwards, looping the Southern Antarctic Circumpolar Current front (SACCF) anticyclonically around the island before being retroflected to the east, causing a Weddell – Scotia confluence around the eastern and northern flanks of the island (see figure 2.2) (Meredith *et al.* 2005; Thorpe *et al.* 2002; Ward *et al.* 2002). These currents are thought to have an effect on the South Georgia ecosystem through influencing the productivity of the ocean waters (Thorpe *et al.* 2002).

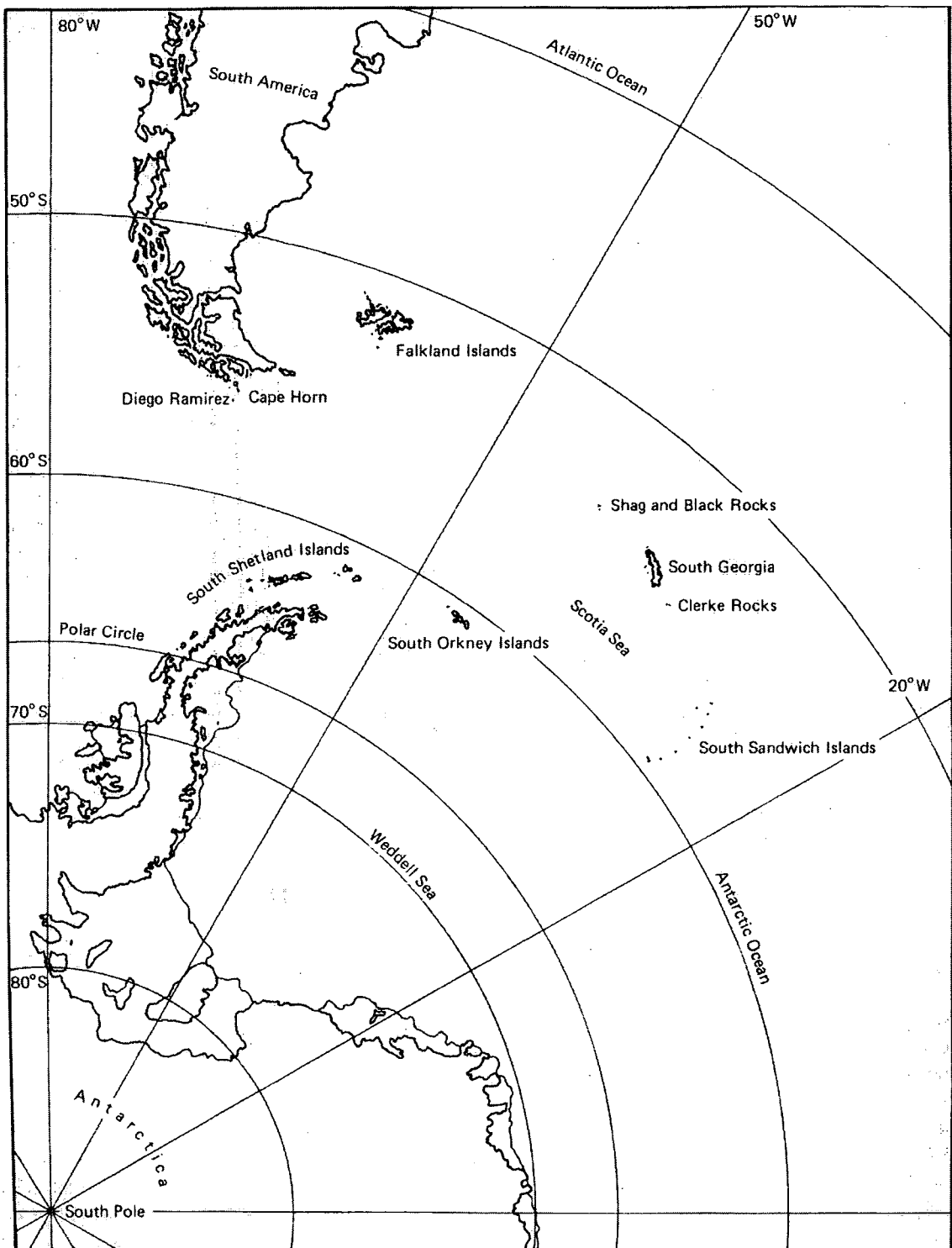


Figure 2.1: South Georgia in relation to South America and the Antarctic Peninsula.

Source: Headland (1984: 2).

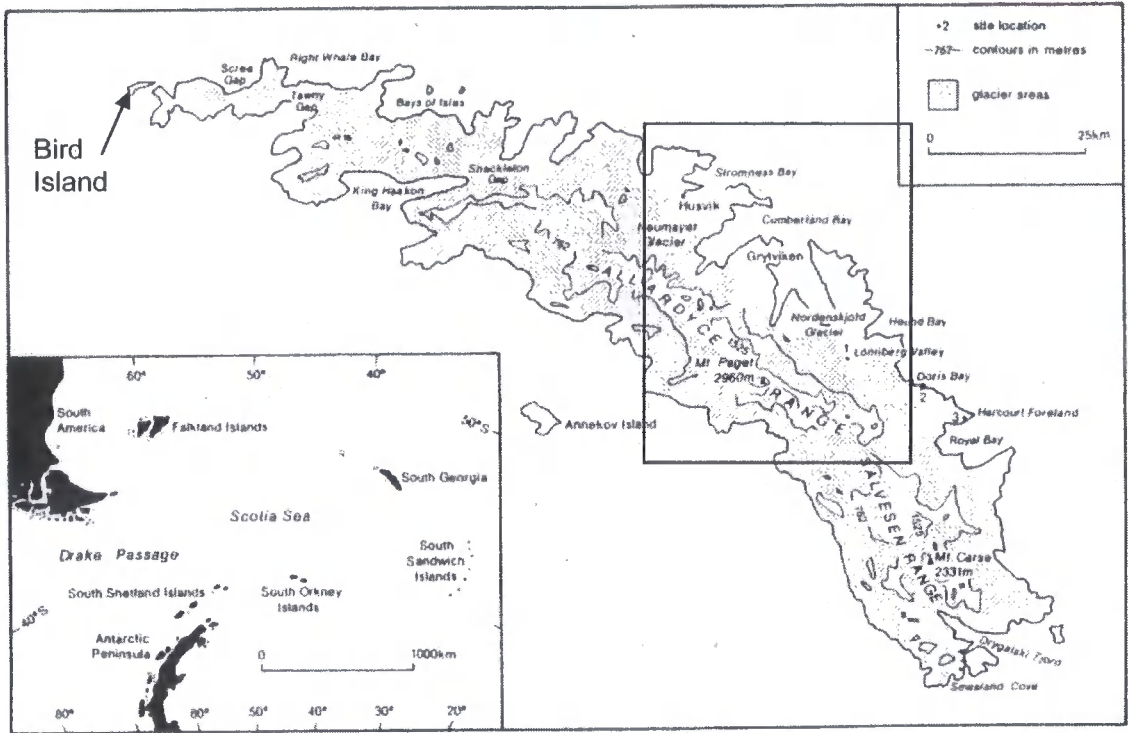


Figure 2.1.1: South Georgia and surrounding islands. The area in the square is shown in more detail in figure 2.3. Source: Clapperton *et al.* (1970)

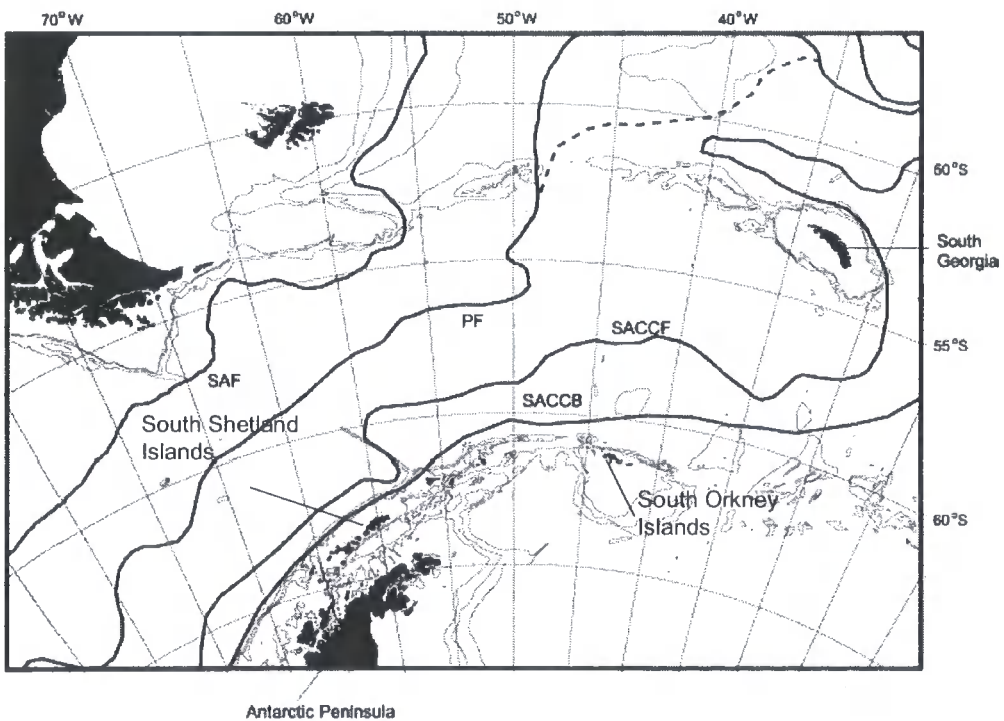


Figure 2.2: Scotia Sea region showing South Georgia and key oceanographic features. Sub-Antarctic front (SAF), Polar Front (PF) (dashed line indicates the position of the Polar Frontal Zone), and the Southern Antarctic Circumpolar Current Front and Boundary (SACCF; SACCB). (Source: Murphy and Reid 2001)

### 2.2.2 Maiviken

Humic lake cored in this study is located in the Maiviken area of the island (see figure 2.4). Maiviken ( $54^{\circ}15'S$ ,  $36^{\circ}30'W$ ) is the name given to a small bay in the headland (Sappho Point) that separates Cumberland West Bay and Cumberland East Bay (see figure 2.3) on the north eastern side of the island. The bay faces north north east, and along its western margin are steep rock walls forming the shoulder of the glacially scoured valley. Along its eastern and southern margins there are a number of small lakes (Evans Lake, Humic Lake, Arch pond and Loken pond). These lakes are located in a narrow low relief area between the bay and the high ridge forming Sappho Point. To the south the land rises to a larger lake, Maivatn and a col that separates Maiviken from the Bore Valley (see figure 2.4).

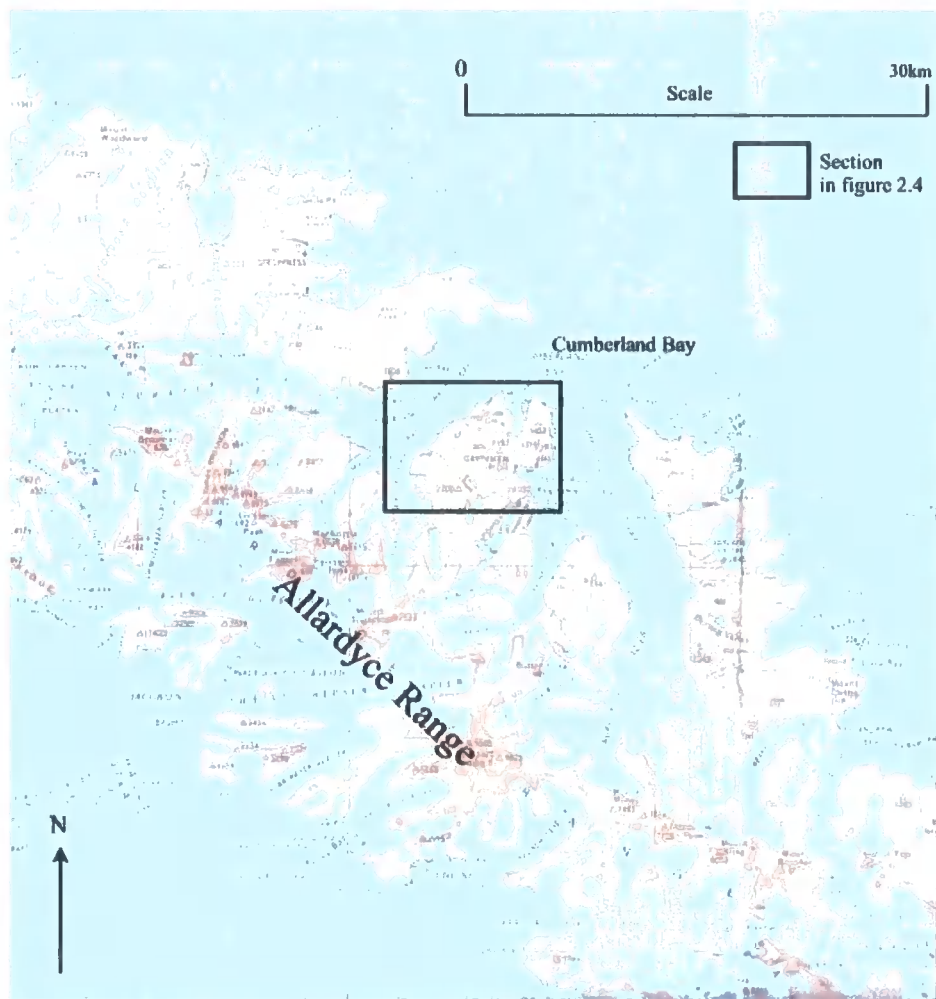


Figure 2.3: Central South Georgia. The area in the square is the Maiviken region and is detailed in figure 2.4. Adapted from DOS (1958)

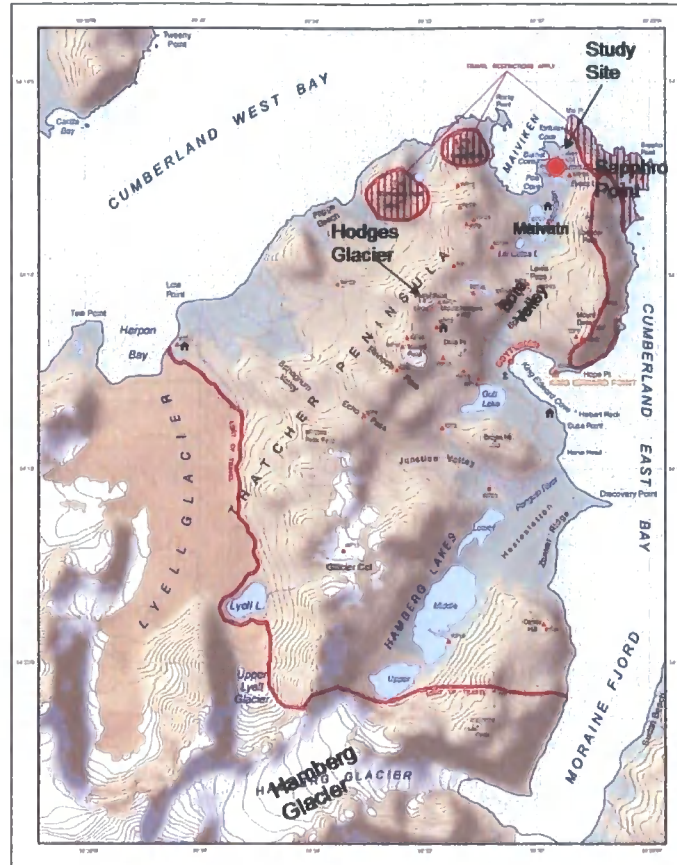


Figure 2.4: Location of the study site in relation to Maiviken and Grytviken. Adapted from Clapperton *et al.* (1970). Map courtesy of Peter Fretwell, Mapping and Geographic Information Centre, British Antarctic Survey, 2006.

The valley was glacially scoured during the retreat of the ice cap at the last glacial maximum, thought to have occurred c. 9700  $^{14}\text{C}$  years BP (Van der Putten and Verbruggen 2005). The relief of the valley is typical of a glacially scored landscape, primarily knob and tarn topography (Sugden and Clapperton 1977). Glacial scouring has formed the steep rock wall which forms the shoulder of the glacially scoured valley. The knob and tarn topography in the valley has resulted in the formation of the numerous lakes (Evans Lake, Humic Lake, Arch pond and Loken pond) (Sugden and Clapperton 1977).

Evidence from peat formations and glacial features suggests that that Maiviken has been ice free throughout the Holocene (Smith 1981) although the presence of glaciers today and the variety of glacial geomorphology indicates that glaciers have fluctuated in the Grytviken region following deglaciation in the early Holocene. The largest glacier in the area is the Hamberg Glacier (see figure 2.5). Although at present it drains into Moraine

Fjord, the presence of roche moutonnées, moraines and glacial tills suggests that it has previously been more extensive and drained into the Cumberland East Bay south of King Edward Cove (see figures 2.5; 2.6). Further north, the Hodges Glacier (see figure 2.5) flowed south east, draining into King Edward Cove. More recently, Hayward (1983) documents the movement of the glacier in the 20<sup>th</sup> Century. From 1955 – 1974 the glacier retreated 5 metres, however, due to the orientation of the glacier and the restraints of Mount Hodges, these fluctuations would affect fluvial and glacial systems in King Edward Cove rather than Maiviken.

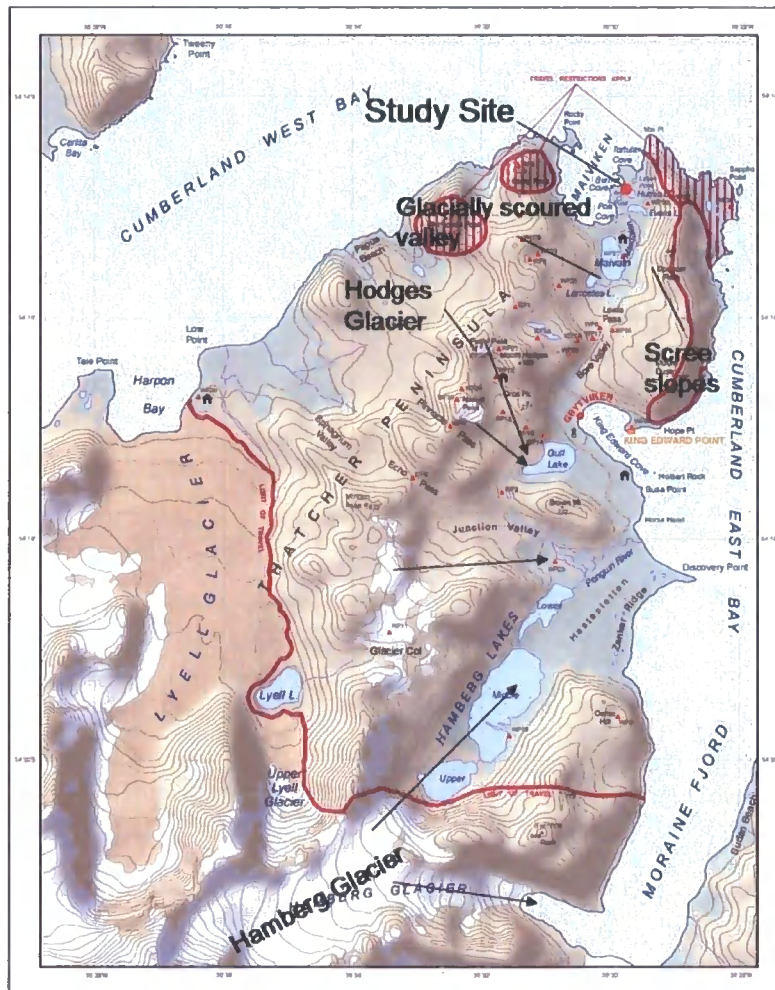


Figure 2.5: The location of the study site relative to the geomorphology of the Thatcher Peninsula. Black arrows indicate glacier flow following the LGM. Map courtesy of Peter Fretwell, Mapping and Geographic Information Centre, British Antarctic Survey, 2006.

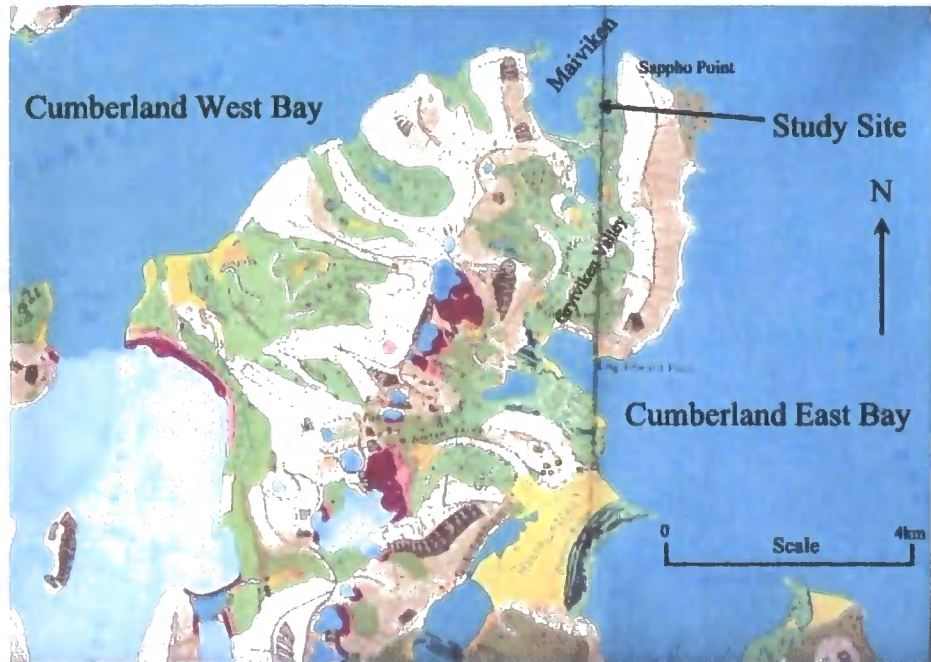


Figure 2.6: Geomorphological map of Maiviken area. Adapted from Clapperton *et al.* (1970)

To the North of the Hodges Glacier, a smaller unnamed glacier is located close to the peak of Mt Hodges. It is possible that during colder periods this advanced into the Bore Valley and drained into Maiviken. In addition to this, there are a number of cirques and cirque glaciers to the east and west of the valley (see figure 2.6). These drain into Lancetes Lake and Maivatn lake south of the study site prior to draining into Maiviken via Maidalen. Without further analysis it is difficult to determine the extent of these glaciers and the movement of these glaciers throughout the Holocene. However, it is thought that glaciation did not reach Evans lake catchment described in Birnie (1990), which is closer in proximity to the Hamberg glacier or Hodges glacier than Humic lake.

The valley where Humic lake is located been formed during a past glacial period. Due to the altitude of the valley it is possible that due to the isostatic uplift that part of the valley was below sea level for some of the Holocene and the lake has formed recently. Without the reconstruction of relative sea level curves in this region this is difficult to quantify, however, it must be considered in analysis as this will have an impact upon the depositional processes operating within the lake.

### 2.2.3 Lake Catchment

Lake Humic cored in this study is approximately 250 metres long and 150 metres wide, located at low altitude (c. 15-20 m) (see figure 2.5; 2.6). The lake and its catchment are ice and snow covered for 4-5 months of the year, but the lake is thoroughly mixed when ice free (Moreton *et al.* 2004). In the lake there are 2 small islands and the water depth reaches 3.5 metres at the deepest point. Several small streams flow into the lake from a closed catchment that measures approximately 400 metres by 300 metres and the lake drains c. 100 m into Maiviken bay from its NW corner. As shown in figure 2.5, Maidalen drains the Bore Valley catchment to the south of the study site, hence, Humic lake is closed isolated catchment and not influenced directly by processes and sediment in the wider Maiviken area. The catchment is bounded to the east by a large ridge, which terminates at Sappho Point (see figure 2.5). This ridge reaches a height of 1050 metres and is thought to be the shoulder of a glacially eroded valley, composed of quartzose greywackes, volcanic greywackes, igneous intrusions and slate (Clapperton *et al.* 1989). At present the ridge is a steep scree slope (see figure 2.7) and a major sediment source for the catchment. The remaining catchment area is knob and tarn topography and is 100 percent vegetated, predominately with tussock grass (see figure 2.5; 2.6). The area around the lake is an areally-scoured landscape of mounds and small hollows, which become water filled during periods of high precipitation.

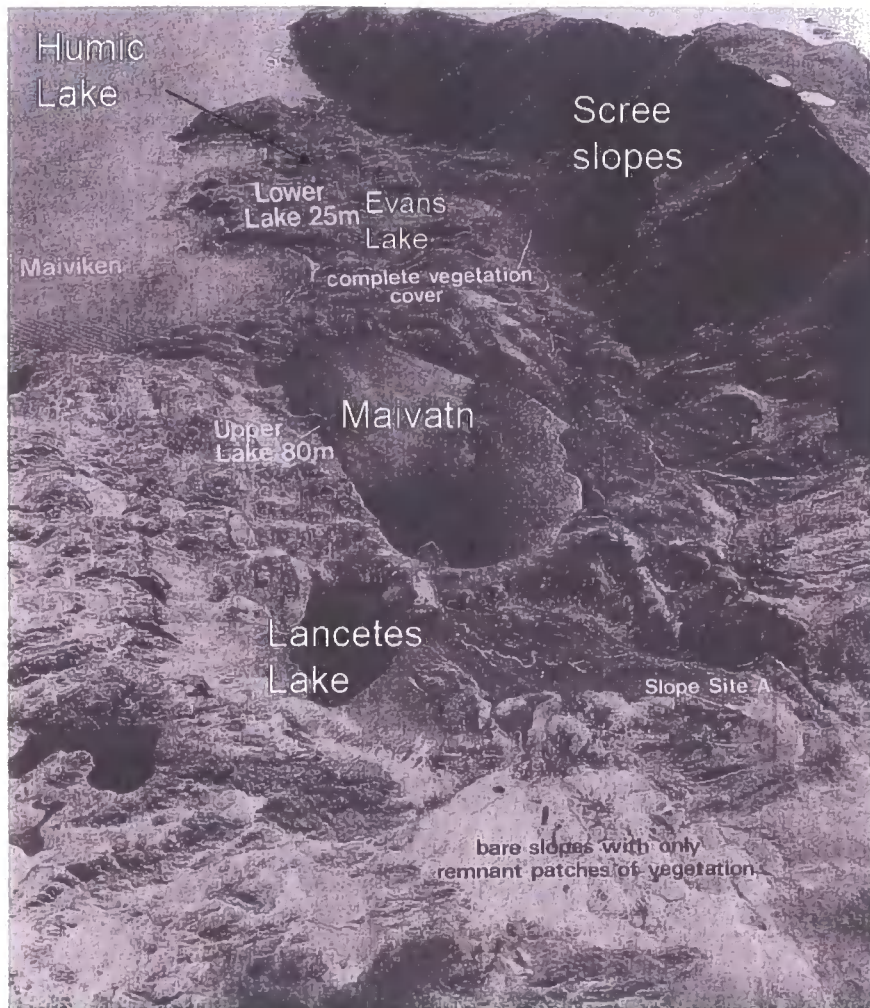


Figure 2.7: An aerial view of the study site catchment. Source: Clapperton *et al.* (1990)



Figure 2.8: The view from the lake towards Grytviken Valley. The snow-covered top of Mt Paget can be seen in the background. The figure illustrates the vegetation type and cover of the lake catchment during the summer.

#### 2.2.4 Core Site

The cores were taken from a location between the central island and a small embayment on the eastern shore (figure 2.9 and 2.10), where the water reached a depth of c. 3.5 m. Two types of corer were used to ensure that both the sediment-water interface was intact and to allow the maximum possible depth to be reached. The first core was taken using a Kullenberg corer to ensure the sediment-water interface was sampled. This core reached a depth of 100 cm, thus, necessitating the use of a modified piston corer to extract the lower core sediment (100-300 cm), as this reaches to greater depths but does not preserve the sediment-water interface as effectively as the Kullenberg corer. The piston corer consisted of a large diameter plastic pipe with tight-fitting piston that was locked by a cable clamp when the core reached the sediment surface. The pipe was then driven into the sediment using a large shaped weight lifted and dropped on a rope (Rosqvist *et al.* 1999).

The core site was chosen in a location closest to the deepest section of the lake as possible to ensure that the sediment was representative of the lake and any changes in sedimentation within the lake as a result of differing currents were not sampled hence, ensuring the core was not misrepresentative of the lake.



Figure 2.9: Retrieving the core, showing the location of the core in the lake. One of the small islands in the lake can be seen in the background.



Figure 2.10: A view of the lake used in the study, looking north across Maiviken. The red crosses show the position of the cores. Figure 2.9 was taken looking from the right of this picture across to the island on the far left of this picture. Source: Sugden and Clapperton (1977)

### 2.2.5 Lake processes

To fully understand the processes operating at the site and therefore the mechanisms in which the sediment has been deposited and the effects this will have upon fur seal hair entrainment and deposition, the lake inputs, outputs and circulation must be evaluated. These processes are key to understanding the changing processes operating within the lake over time and the effect this may have upon the fur seal hair record.

#### 2.2.5.1 Lake inputs

The primary inputs into the lake are at present fluvial and slope processes which transport precipitation and surface run off from the localised catchment. This surface run off is likely to transport clastic sediments from the scree slopes to the east of the catchment (see figure 2.7). In addition to this, vegetation debris and soils become entrained and are washed into the lake. Other elements in the catchment such as fur seal hairs and excrement will also be entrained in surface run off and enter the lake catchment. Furthermore, fur seal populations wallowing in the lake will entrain sediment, further increasing the inputs. Aeolian processes may also transport some sediment from off shore winds, however, these are likely to be minimal due to the

sheltered nature of the lake and will be minor in comparison to the sediment input from fluvial and slope processes.

From the discussion in section 2.2.2, it is clear that glacial processes are not influencing the sediment transport and input into the lake today. Although this may have been a sediment pathway previously when glacier extent was greater, evidence presented in section 2.2.2 suggests this is unlikely to be a major sediment source as the glaciers draining into the Bore Valley, drain into Maivatn to the south (and upstream) of the catchment which therefore, is likely to intercept most sediment.

The lake and catchment are snow and ice covered for approximately 4 – 5 months of the year, although due to the relatively mild climate at South Georgia, the lake ice does not reach a thickness where it is likely to freeze to, or disturb, the lakefloor sediment. Due to this ice and snow cover, direct sediment input is restricted during the winter period and there is likely to be very little activity in the catchment or the lake at this time. Snow and ice melt as the climate ameliorates in the spring and summer months transports a rapid flux of sediment into the lake.

#### 2.2.5.2 Lake circulation

Without sediment traps within the lake, the lake circulation and affect this will have on sediment distribution sediment retention in the lake cannot be fully evaluated. However, due to the sheltered location of the lake and proximity relative to glacial activity, it is thought that lake mixing and sediment disturbance is minimal. As the lake is ice covered for 4 -5 months of the year and the lake is too deep to permit basal freezing, there are very few factors that would affect sediment deposition and retention in the lake during this period. In the summer months, fur seals wallow in the lakes, however, this is on the surface of the lake and is unlikely to significantly affect the basal sediments. As discussed above, the sediment cores were taken from the deepest point in the lake to reduce any potential effect of sediment disturbance.

#### 2.2.5.3 Lake outputs

The lake output is primarily via the outlet, which drains ~100 metres to the sea. Flow in this outlet is not rapid, suggesting sediment transport from the lake is minimal and the majority is retained and deposited within the lake catchment. Analysis of the sediment

core and sedimentation rate will provide a greater understanding of the retention of the sediment within the catchment.

### 2.3 Late Holocene Environmental Changes

This section examines Late Holocene Environmental Changes at a firstly on South Georgia as a whole and then using this evidence associated with more site specific reconstructions, catchment environmental changes are evaluated. Finally the environmental changes in the Antarctic region are determined. This evaluation at varying scales is important to fully understand the processes operating within the catchment. Evaluating the climate changes on South Georgia with regional environmental change can provide an indication of the changes in ocean and atmospheric circulation in the region and help to define the causal mechanisms for such changes (Jones *et al.* 2000).

The location of South Georgia 250 km south of the Polar Front, is key in comprehending the climate of the island. This location close to the Polar frontal boundary allows the movement of the Polar Front to be tracked and hence, records the effect this has upon the climate connections in temperate and polar environments to be evaluated (Van der Putten 2004; Rosqvist and Schuber 2003). Although this is recognised as a key area of research, studies implemented at South Georgia have been restricted primarily due to the numerous limitations of proxies in this harsh environment. Firstly, the use of pollen assemblages as a proxy is limited as only two genera of pollen (*Gramineae* and *Acaena*) account for 90% of the total pollen count therefore; these species have widespread dominance (Barrow 1978; Clapperton *et al.* 1989; Van der Putten 2004). Very little is known about minor species as the modern ecology is poorly known and inhospitable conditions make further research difficult (Birnie 1990). Secondly, the wide ecological tolerance of these species restricts the extent to which past environmental change can be reconstructed (Barrow and Lewis-Smith 1983; Barrow 1978). Thirdly, a large number of pollen grains are blown across the Southern Ocean from South America and are deposited on South Georgia, hence, what may appear as climatic change may actually only reflect changes in southern westerlies or the influence of local topographic features on air currents and hence, the use of pollen assemblages in environmental reconstruction at South Georgia can be misinterpreted (Barrow and Lewis-Smith 1983).

Despite these problems in reconstructing the climate of South Georgia, it is recognised that South Georgia has experienced a range of climatic conditions through the Holocene. From the use of different proxies to reconstruct environmental change, it is clear that the environmental response is not uniform and often evidence is conflicting as different proxies highlight the following different elements of environmental change. Firstly temperature affects the climate and influences the catchment in terms of the duration of the ice cover and the vegetation within the catchment. On South Georgia, Van der Putten (2004) and Barrow (1983) provide an account of the relative temperature changes on the island through the late Holocene. Secondly, precipitation has an influence upon the climate and the catchment regime. Precipitation can influence the vegetation cover, however, it also influences the glacial activity and greatly influences the inputs and outputs of the lake. Precipitation has been inferred through the late Holocene on South Georgia from pollen and macrofossil records (Barrow and Lewis Smith 1983). Finally, glacial activity; temperature is the most influential factor affecting glacier regime, however, fluctuations in precipitation also affect the mass balance of the glacier, thus, a decrease in temperature may not reflect a glacial advance if precipitation input is insufficient (Clapperton 1990). In addition to this, a number of glaciers on South Georgia are fjord glaciers; these are unreliable for dating climatically forced advances as response lags can be up to 100 years (Clapperton and Sugden 1988). However, it is essential to understand these glacial regimes specifically on a local scale as glacial process influence geomorphology and consequently sediment transport processes in the catchment.

Using a combination of proxies allows the significant climate episodes to be more clearly understood and permits response times of different systems to be recognised, hence, reducing error and providing a more accurate picture of environmental change (Clapperton *et al.* 1989). Previous studies at South Georgia have used a range of proxies that include macrofossils (Van der Putten 2004; Taylor *et al.* 2001), glacier fluctuations (Clapperton and Sugden 1988; Clapperton *et al.* 1989), biogenic silica (Rosqvist *et al.* 1999), diatom assemblages (Van der Vijver 1996) and pollen assemblages (Birnie 1990; Barrow 1978; 1983a; 1983b; 1983c) and finally radiocarbon dates from peat layers have been used to indicate the duration of vegetation development (Van der Putten 2005, Gordon 1987). These different proxies will be evaluated and used to reconstruct the climate of the catchment at Maiviken, the South Georgian climate and the sub Antarctic

climate through the late Holocene. Figure 2.11 summarises the climate of South Georgia in terms of temperature, precipitation and glacial activity from analysis of these proxy records.

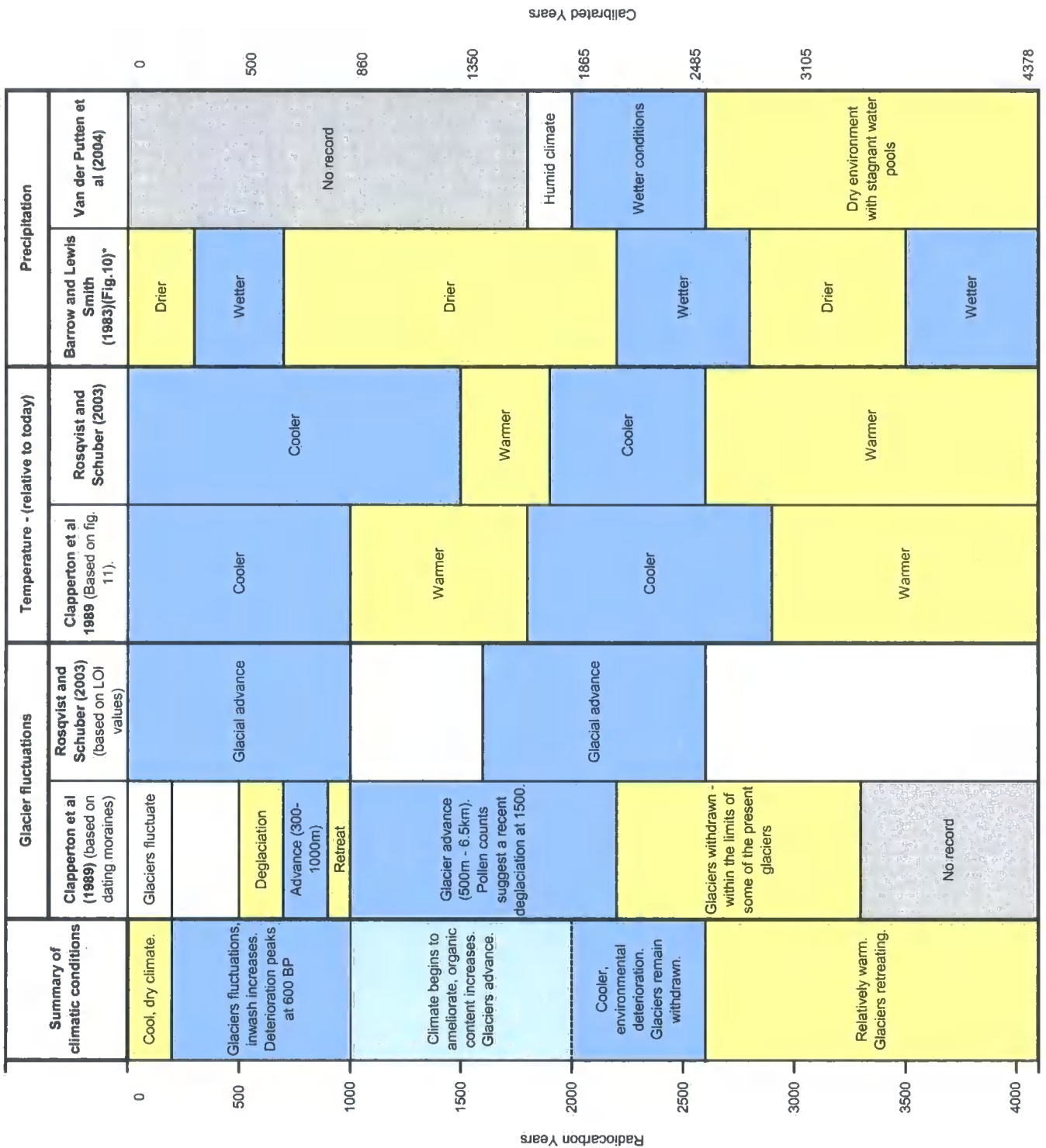


Figure 2.11: A summary of the climate at South Georgia through the late Holocene.

### 2.3.1 South Georgia Environmental Change

It is widely agreed that in South Georgia deglaciation culminated approximately 10,000  $^{14}\text{C}$  years BP, as many species of flora became established (Van der Putten 2004; Clapperton *et al.* 1989; Barrow 1978). Deglaciation was followed by climate amelioration, peaking at 5600-4800  $^{14}\text{C}$  yrs BP (6350-5500 cal yrs BP) and conditions were more conducive to plant growth than today as pollen assemblages suggest temperatures were 0.6°C warmer than present (Birnie 1990; Clapperton 1989). During the late Holocene, significant climate deterioration occurred around 2500  $^{14}\text{C}$  yrs BP (2500 cal yrs BP) and again at 600  $^{14}\text{C}$  yrs BP (540 cal yrs BP) (see figure 2.11) (Clapperton and Sugden 1988; Van der Putten 2004).

#### 2.3.1.1 Pre 2600 $^{14}\text{C}$ years BP

Climate changes inferred from pollen and diatom assemblages in lake sediments taken from the Maiviken region suggest that warmer conditions persisted from 3300  $^{14}\text{C}$  yrs BP (3500 cal yrs BP) until 2800  $^{14}\text{C}$  yrs BP (2800 cal yrs BP) (Birnie 1990). This climate amelioration and restricted ice cover is supported by evidence from microfossil and pollen records. These records suggest a drier period from 4000  $^{14}\text{C}$  yrs BP to 2600  $^{14}\text{C}$  yrs BP (4400- 2600 cal yrs BP), similar and possibly warmer than the present day climate, often referred to as the Late Holocene Climate Optimum (Van der Putten *et al.* 2004; Rosqvist and Schuber 2004; Barrow 1978). This climate amelioration is further supported by evidence from peat layers on glacial moraines to suggest that glacier extent was restricted from 3330  $^{14}\text{C}$  yrs BP to 2230  $^{14}\text{C}$  yrs BP (Gordon 1987; Clapperton *et al.* 1989). Although the exact timing of this change differs, a large body of evidence suggests that the period prior to 2600  $^{14}\text{C}$  yrs (2600 cal yrs BP) was as warm or warmer than today.

#### 2.3.1.2 2600- 1600 $^{14}\text{C}$ yrs BP

Birnie (1990) suggests that the climatic optimum began to deteriorate at 2900  $^{14}\text{C}$  years BP as the minerogenic content in the lake cores increases and from 2600  $^{14}\text{C}$  years BP the climate was wetter. This coupled with an increase in oligotrophic bogs at 2600  $^{14}\text{C}$

years BP (2600 cal years BP), provides a broad line of evidence to suggest that the Late Holocene Climate Optimum had ceased by 2600  $^{14}\text{C}$  years BP as the climate cooled and precipitation increased (Van der Putten 2004; Rosqvist and Schuber 2004).

Glaciological evidence also supports this climate deterioration and increase in precipitation as glaciers began to advance at 2200  $^{14}\text{C}$  years BP (2200 cal yrs BP) (Rosqvist and Schuber 2004; Clapperton 1990; Clapperton and Sugden 1988). This climatic shift is further supported by radiocarbon dates from peat layers and moraines, which imply ice-free conditions had ceased by 2230  $^{14}\text{C}$  years BP (3500-2200 cal yrs BP) (Gordon 1987; Van der Putten 2005)

In terms of the vegetation cover, evidence from pollen assemblages suggests that since deglaciation, conditions have not been harsh enough to prevent the survival of the woody herb genus *Acaena* (indicative of a warm, dry climate) for long periods (see figure 2.15) (Barrow 1978). Birnie (1990) provides a pollen assemblage to suggest that this phase (2600-1600  $^{14}\text{C}$  years BP) was similar to the present day climate at South Georgia, however, Clapperton's (1990) glaciological evidence suggests a cooling of 0.5-1°C. Although the magnitude of the change is debatable, it is clear that the climate deteriorated after 2600  $^{14}\text{C}$  years BP (2600 cal yrs BP), and is thought to be 'the most striking event in the Holocene palaeoclimatological history of South Georgia', with major changes in atmospheric and oceanographic circulation (Van der Putten 2004: 390).

The culmination of this period of climatic deterioration is not frequently documented in the literature and it is likely that the change was gradual. Although pollen assemblages suggest the climate began to ameliorate at 2000  $^{14}\text{C}$  years BP, the high content of silt and clay and loss on ignition (LOI) values in lake cores suggest the climate remained relatively cool until 1600  $^{14}\text{C}$  years BP (Barrow 1978; Birnie 1990).

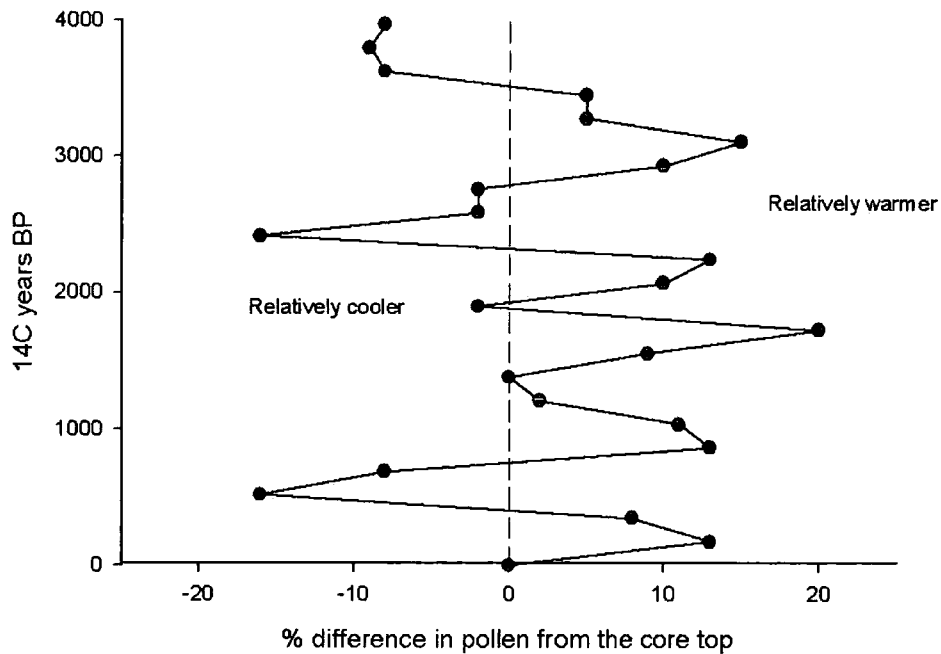


Figure 2.12: Relative temperatures at South Georgia through the late Holocene in comparison to the climate today. Values were calculated from pollen assemblages of Gramineae and Acaena in Barrow (1978). Relative temperatures were calculated from the percentage of Gramineae and Acaena today, with Gramineae indicating a warmer climate and Acaena indicating a warmer climate than today. The scale is the difference in percentage of Gramineae and Acaena between the sample and the percentage at the top of the core (i.e. the climate today). For example, positive 20 indicates at that point in the core there was 20% more Acaena than found in the top sample. A negative 20 indicates 20 more Gramineae in the sample than in the top of the core. The age of the sample was calculated from a radiocarbon date at the base of the core.

### 2.3.1.3 1000 <sup>14</sup>C years BP

The next period of environmental change began around 1000 <sup>14</sup>C years BP (850 cal yrs BP) as LOI values indicate a cooling (Rosqvist and Schuber 2003). Evidence from lake sediments suggest that deterioration peaked at 600 <sup>14</sup>C years BP as minerogenic content in the lake increased (Birnie 1990). Associated with this deterioration are glacial fluctuations, suggesting the period from 600 <sup>14</sup>C years BP was particularly cold and wet (Clapperton *et al.* 1989; Rosqvist and Schuber 2003). This peak in cooling is further

supported by evidence from peat layers which indicates that peat growth increased from 990  $^{14}\text{C}$  years BP (838 cal yrs BP) to 775  $^{14}\text{C}$  years BP (686 cal yrs BP), suggesting a warmer interval after which the climate deteriorated.

#### 2.3.1.4 Post 200 $^{14}\text{C}$ years BP

This climatic deterioration lasted until approximately 200  $^{14}\text{C}$  yrs BP (200 cal yrs BP) when the climate ameliorated and glaciers began to advance (Clapperton *et al.* 1989; Birnie 1990). Small glacier expansion occurred during the 19<sup>th</sup> century, forming multiple moraines suggesting complex oscillations of glacier margins (Birnie 1990). This was followed by readvances during the 1920's and glacier retreat until the late 1940's, after which all glaciers have been receding (Clapperton and Sugden 1988). Although this record suggests marked glacier fluctuations, these fluctuations reflect localised conditions and are dependant upon glacier type and form, thus, cannot be solely used to evaluate climate (Hayward 1983). It is thought that climatic conditions only significantly improved within the last 50 years, with the climate becoming warmer and wetter (Birnie 1990). This climate amelioration is supported by the 5 metre retreat of the Hodges glacier, south west of the catchment (see figure 2.5; 2.6) (Hayward 1983).

#### 2.3.2 Humic Lake Environmental Changes

The catchment geology and geomorphology has evolved throughout the late Holocene in response to local and regional climate changes. To fully understand the mechanisms by which the fur seal hairs are incorporated into the lake sediments and the effect any changes may have upon the entrainment and preservation of fur seal hairs in the sediment, the differing lake inputs and depositional processes through the Holocene must be comprehended. Although there are a variety of climatic variables affecting the catchment, the primary factors affecting sediment transport processes can be defined as the catchment stability and vegetation cover and hence, catchment environmental changes will be evaluated under these factors.

Past studies, specifically Clapperton *et al.* (1989) and Birnie (1990) have used palaeolimnology to analyse the climate of Maiviken area through the late Holocene. Although these catchment characteristics can be determined with analysis of the core in

this study, additional proxies provide a more robust estimate of the climate changes occurring during the late Holocene. Figure 2.13 summarises the climate changes in the Maiviken area. Differing proxies provide evidence for differing catchment conditions. To understand the impact this has upon sediment composition and transport mechanisms, figure 2.13 defines the proxy records having an effect on the catchment stability and vegetation cover to determine the processes operating within the catchment relative to the wider climatic changes.

The summary presented in figure 2.13 considers the findings primarily by Birnie (1990) as this paper was based on lake sediment cores in close proximity to the Humic lake catchment and uses a multifaceted approach using sediment description, pollen and spore analysis and microfossil analysis to determine past environmental change. To supplement this record, further evidence will be summarised from Barrow (1983). This record uses micropollen analysis to evaluate the vegetation changes and identify warm and cold periods during the Late Holocene. However, as discussed in earlier sections, this record has inherent errors related to the variability of the pollen in this region and therefore cannot be used as a sole indicator of climate change in this region. Additional studies (Van der Putten 2005; Rosqvist and Schuber (2003)) are also used in analysis to provide an indication of the catchment stability or vegetation cover on South Georgia, however, these are not site specific.

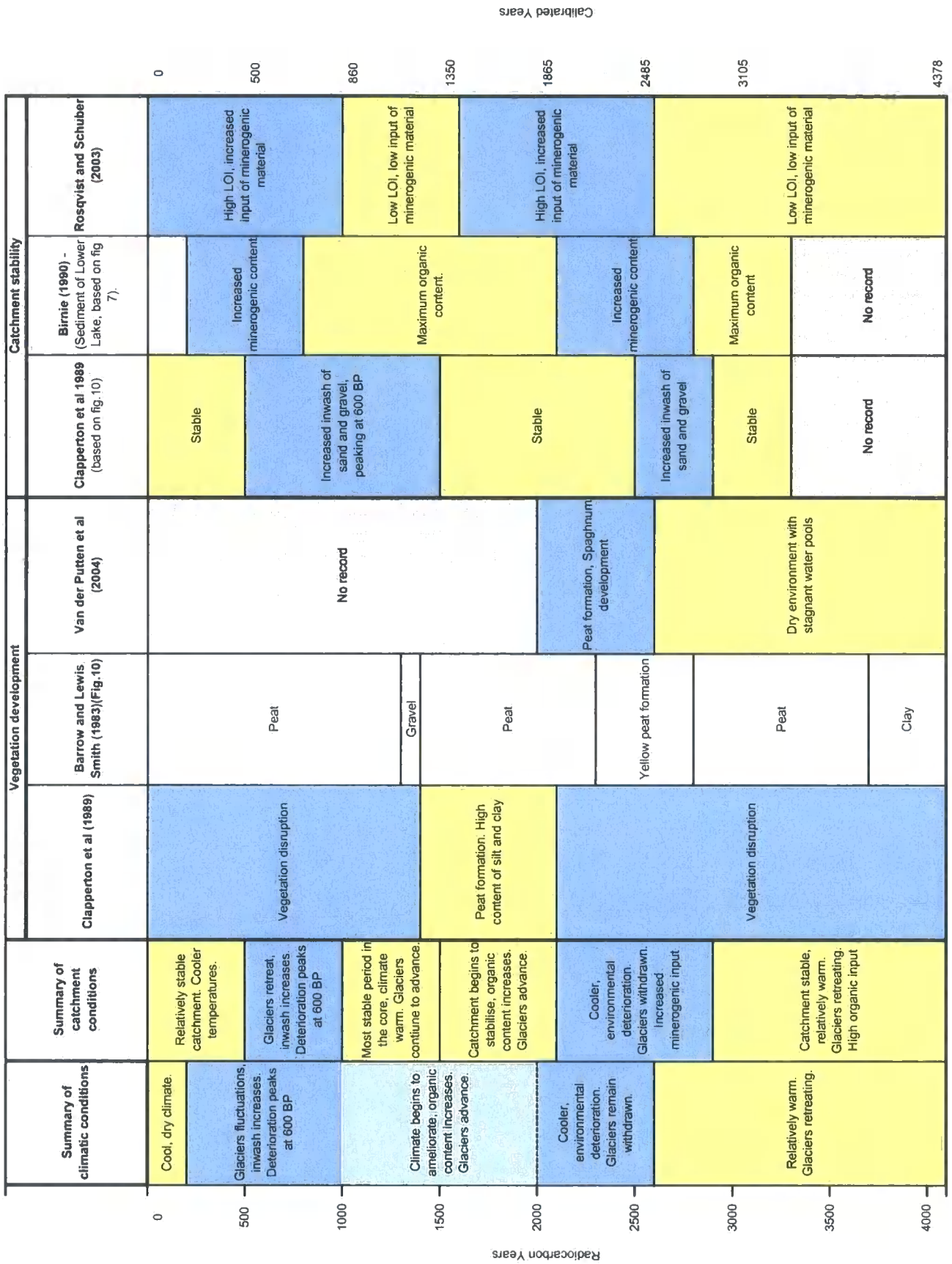


Figure 2.13: A summary of late Holocene environmental changes in the Maiviken catchment.

### 2.3.2.1 General climate

Birnie's (1990) paper analyses a core from Lake Maivatn and Evans Lake (see figure 2.7). A date of 8657  $^{14}\text{C}$  yrs BP at the base of the core indicates that the catchment of Evans Lake has been vegetated throughout the record. From this evidence it can be inferred that due to the close proximity of the Humic lake and the lower latitude, the catchment has been ice free and vegetated for the majority of the late Holocene. From this evidence it can be assumed that the catchment has remained relatively stable during the late Holocene and there is no evidence to suggest the geology and geomorphology of the catchment has changed dramatically since the LGM and therefore will not have had a significant impact upon the fur seal hair deposition or lake sediment dynamics.

### 2.3.2.2 Catchment specific environmental changes

- Pre 2900  $^{14}\text{C}$  yrs BP (*Pre 2600  $^{14}\text{C}$  yrs BP*)

This relatively warm period documented on South Georgia (see figure 2.13) caused increase vegetation cover and as documented in Birnie (1990) an increase in organic input in the lake catchment. This is further supported by pollen analysis which indicates peat development prior to 2700  $^{14}\text{C}$  yrs BP (Birnie 1990). Increased vegetation cover and a warm climate suggests a stable catchment where inputs are likely to be minimal. Comparing this to the climate record from South Georgia, it appears this climatic optimum ceased earlier in the catchment than in other areas on South Georgia, however, this can be attributed to slight dating errors or the maritime location of the study site.

- 2900-2100  $^{14}\text{C}$  yrs BP (*Climate deterioration 2600  $^{14}\text{C}$  yrs BP*)

Although changes in diatoms often reflect changes in lake chemistry rather than a change in temperate, the presence of two new types of Diatom species in the lake record at 2600  $^{14}\text{C}$  yrs BP coupled with a change in stratigraphy suggests a cooling (Birnie 1990). Associated with this cooling is a decline in vegetation cover, decreasing catchment stability and increasing minerogenic inputs into the lake.

- 2100-1000  $^{14}\text{C}$  yrs BP (2600 – 1600  $^{14}\text{C}$  yrs BP)

The presence of Compositae pollen at 2000  $^{14}\text{C}$  yrs BP suggests a climatic warming and associated increase in vegetation cover (Birnie 1990). Clapperton *et al.* (1989) indicate that glacier expansion occurred during this period, although there are no glaciers located in the catchment, this advance suggests an increase in precipitation and decrease in catchment stability, hence, increasing the inputs into the lake. From this evidence, it is likely that this period, although warmer than 2600  $^{14}\text{C}$  yrs BP was not as warm as pre 2600  $^{14}\text{C}$  yrs BP.

- 1000 – 500  $^{14}\text{C}$  yrs BP

Evidence presented by Birnie (1990) suggests that by 1000  $^{14}\text{C}$  yrs BP the climate began to deteriorate. An increase in minerogenic sediment in the core indicates a decline in organic content and a decrease in catchment stability. A peak in minerogenic content and increase in palynomorph concentration suggests this cooling and catchment instability peaked at 600  $^{14}\text{C}$  yrs BP. This is further supported by glaciological evidence presented by Clapperton *et al.* (1989).

- 500  $^{14}\text{C}$  yrs BP – Present

From 500  $^{14}\text{C}$  yrs BP to present, proxy records indicate climate amelioration, increased vegetation cover and associated increase in catchment stability (see figure 2.13)

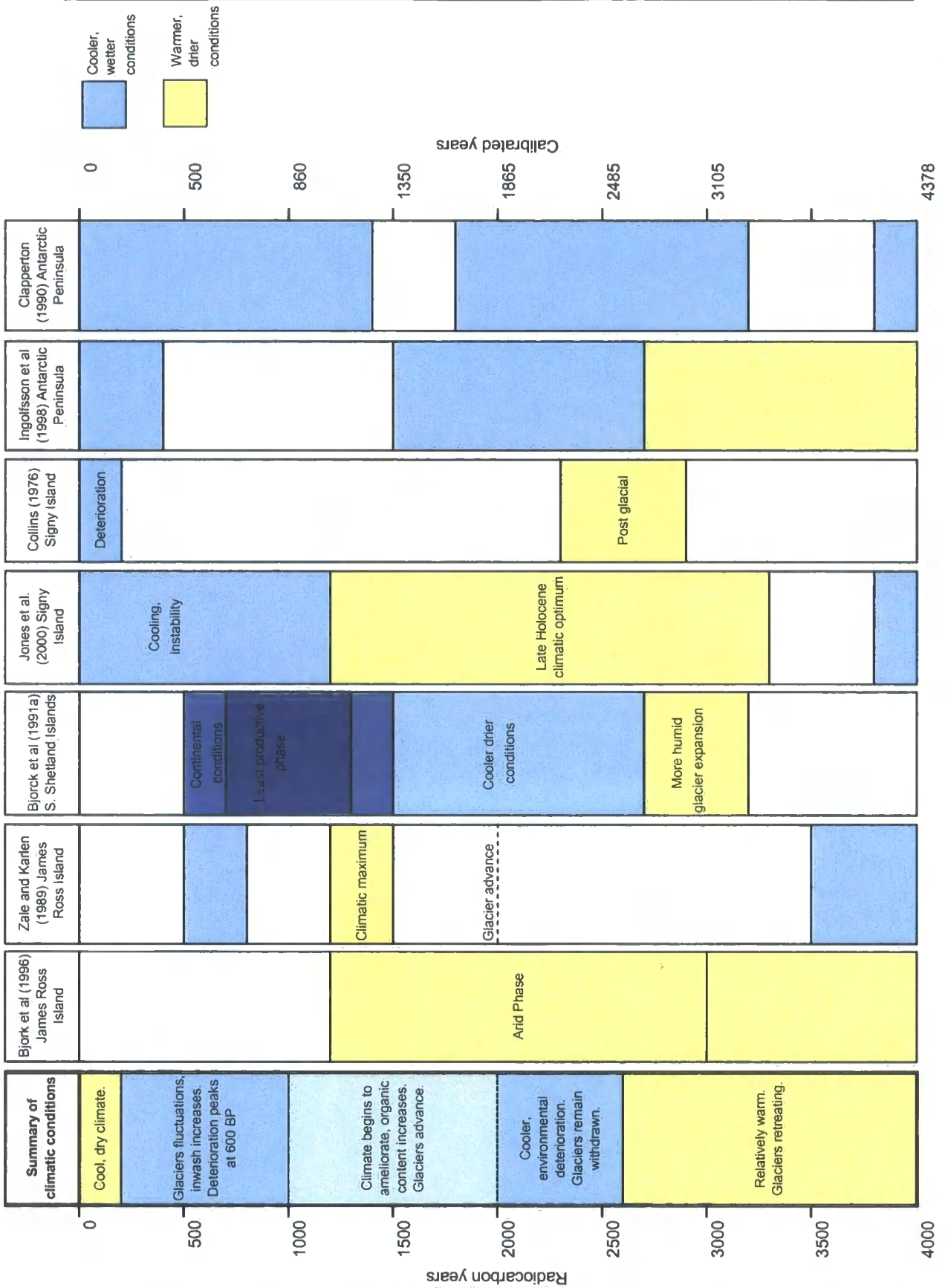


Figure 2.14: A summary of sub Antarctic climate change through the late Holocene.

### 2.3.3 Regional environmental change

It is widely documented that the period from 4700 to 2000  $^{14}\text{C}$  yrs BP was warmer than today (Hodgson *et al.* 2004), although the exact timing of this varies across the Antarctic region. From ice cores in Antarctica, Ciais *et al.* (1994), suggest that a warmer, more stable period occurred from 4500  $^{14}\text{C}$  yrs BP. This period of climatic optimum conditions occurs slightly later on the Antarctic Peninsula, at 4000-3000  $^{14}\text{C}$  yrs BP (4400- 3100 cal yrs BP) and is delayed further on Sub- Antarctic Islands (Ingolfsson *et al.* 1998). Pollen records from lake sediments on Livingston Island, (South Shetland Islands) suggest milder, more humid conditions from 2700  $^{14}\text{C}$  yrs BP (Björck *et al.* 1991a). This period is termed the Mid Holocene Hypsithermal and it is widely recognised that during this period, there was rapid sedimentation, high organic productivity and increased species diversity (Hodgson *et al.* 2004)

#### 2.3.3.1 2600-2000 $^{14}\text{C}$ yrs BP (South Georgia climate deterioration)

Records from the Antarctic Peninsula, Antarctica and the Southern Ocean, indicate a significant climatic shift at 2400  $^{14}\text{C}$  yrs BP (2500 cal yrs BP) (Domack and Mayewski 1999). Marine records from the Antarctic Peninsula suggest that the climate deterioration occurred at 2700  $^{14}\text{C}$  yrs BP causing reduced productivity and more extensive and persistent sea ice (see figure 2.14) (Ingolfsson *et al.* 1998). This correlates with evidence on South Shetland Island, which implies cooler conditions commenced at 2700  $^{14}\text{C}$  yrs BP (2800 cal yrs BP) (Björck *et al.* 1991a). Although this shift occurred slightly earlier in this region than on South Georgia, this may be a result of the lag time within the system and the more northerly location of South Georgia. Although, Hodell *et al.* (2001) provide a correlation of Holocene climate change at Taylor Dome, North Atlantic and the Southern Ocean in which all the records show a significant climate shift at 2500  $^{14}\text{C}$  yrs BP (2500 cal yrs BP). This correlation throughout the Southern Ocean indicates a significant climate change occurred at this time that was likely to be caused by a global forcing mechanism. Domack and Mayewski (1999) identify this climate shift in GISP2 core from Greenland, which indicates a cool episode commencing at 2500  $^{14}\text{C}$  yrs BP (2500 cal yrs BP). Evidence from Chilean records, suggest a less humid phase occurred from 2500  $^{14}\text{C}$  yrs BP (2500 cal yrs BP), suggesting this change in climate at 2500  $^{14}\text{C}$  yrs BP (2500 cal yrs BP) had regional implications and was possibly a result of a regional shift in the position and strength of the Westerlies (Lamy *et al.* 2001).

The climate change widely documented to occur at 2500  $^{14}\text{C}$  yrs BP (2500 cal yrs BP) is not evident in all the records on the Antarctic Peninsula, suggesting the forcing mechanism for this change was of local origin. At James Ross Island, a warmer arid phase commenced at 3000  $^{14}\text{C}$  yrs BP (3100 cal yrs BP) and lasted until 1200  $^{14}\text{C}$  yrs BP (1050 cal yrs BP) (see figure 2.14) (Björck *et al.* 1996; Jones *et al.* 2000). This also correlates with the Palmer Deep record that indicates that from 3000-2000 cal BP conditions were more humid than present with a reduced sea ice extent, with a particularly warm event occurring at 2680 cal BP (Noon *et al.* 2003). Although this warming is not documented in the South Georgia record or in other records from the Antarctic Peninsula, the increase in humidity does correlate with the glacier advance on South Georgia that was delayed after the onset of the climate deterioration, which Noon *et al.* 2003 infer to be related to a northward shift of the Southern Westerlies.

#### 2.3.3.2 2000-1000 $^{14}\text{C}$ yrs BP (South Georgia warm phase)

On the Antarctic Peninsula, glacier advance occurred from 2000  $^{14}\text{C}$  yrs BP (1850 cal yrs BP), suggesting a change in the precipitation regime but not necessarily deterioration (Ingólfsson *et al.* 1998). On the South Shetland Islands, the opposite occurred as Björck *et al.* (1991a) document deterioration from 1300-700  $^{14}\text{C}$  yrs BP (1200-600 cal yrs BP). This is in agreement with records from Antarctic ice cores, which record an important cooling which commenced at 2000  $^{14}\text{C}$  yrs BP (1850 cal yrs BP) and culminated at 1000  $^{14}\text{C}$  yrs BP (850 cal yrs BP) (Ciais *et al.* 1994).

#### 2.3.3.3 1000-200 $^{14}\text{C}$ yrs BP (Cooling, fluctuating climate at South Georgia)

The cooling experienced in South Georgia at 1000  $^{14}\text{C}$  yrs BP (850 cal yrs BP), is also evident in records from the Antarctic Peninsula, Sub Antarctic Islands and ice core records at Taylor Dome (Noon *et al.* 2003; Hodell *et al.* 2001). Cooling commenced first at South Shetland Islands, as Björck *et al.* (1991b) document more continental conditions from 1500- 500  $^{14}\text{C}$  yrs BP, with the coldest period starting at 1300  $^{14}\text{C}$  yrs BP (1200 cal yrs BP) and lasting until 700  $^{14}\text{C}$  yrs BP (600 cal yrs BP). On the Antarctic Peninsula, a cooling of 0.5-1°C began earlier at 1400  $^{14}\text{C}$  yrs BP (1250 cal yrs BP) (Clapperton 1990). This cooling was delayed until 1300  $^{14}\text{C}$  yrs BP (1200 cal yrs BP) on Signy Island, when a deterioration occurred following the long lasting climatic optimum (see figure 2.14) (Jones *et al.* 2000).

The maximum climate deterioration at South Georgia that commenced at 600  $^{14}\text{C}$  yrs BP correlates with regional climate fluctuations. At Signy Island, a relatively warm period ceased at 600  $^{14}\text{C}$  yrs BP. This deterioration is documented earlier on James Ross Island, commencing at 750  $^{14}\text{C}$  yrs BP and lasting until 500  $^{14}\text{C}$  yrs BP (Zale and Karlen 1989). However, these events are not documented on the South Shetland Islands as maximum deterioration commenced at 1300  $^{14}\text{C}$  yrs BP (1200 cal yrs BP) and ceased at 700  $^{14}\text{C}$  yrs BP (600 cal yrs BP) (Björck *et al.* 1991). This fluctuation correlates with evidence from the Antarctic Peninsula, which indicates warming, termed the Medieval Warm Period (MWP) commencing at 1000  $^{14}\text{C}$  yrs BP (850 cal yrs BP), ending at 500  $^{14}\text{C}$  yrs BP with the onset of the Little Ice Age (LIA) (see figure 2.15), documented as the strongest of late Holocene cold and warm periods in the Antarctic Peninsula region (Khim *et al.* 2002).

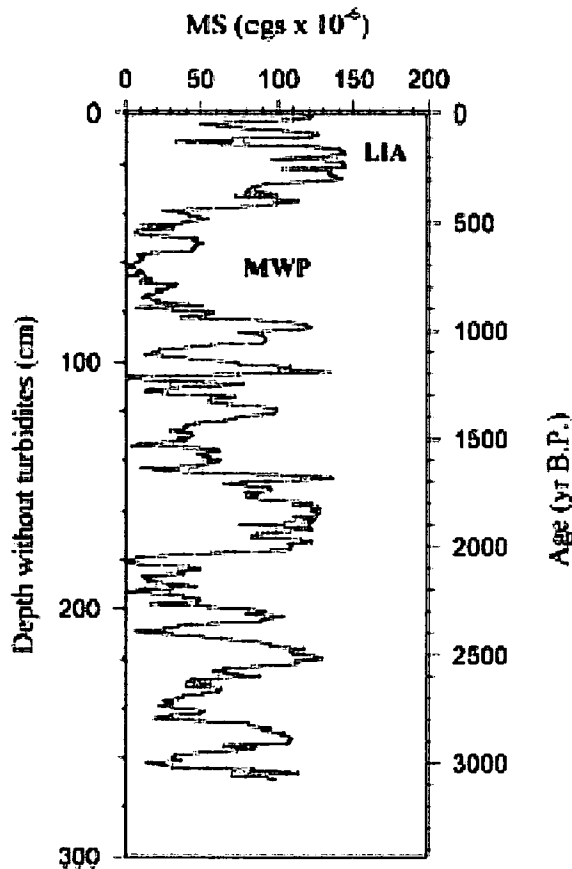


Figure 2.15: A high-resolution magnetic susceptibility record from the Eastern Bransfield Basin, Antarctic Peninsula highlighting the timing of the Little Ice Age (LIA) and the Medieval Warm Period (MWP) in the region. Source: Khim *et al.* (2002: 243).

2.3.3.4 200 <sup>14</sup>C yrs BP

Thompson *et al.* (1994) suggest a cooler period on the Dyer Plateau (Antarctic Peninsula) from 1850-1930 AD when accumulation rates and dust increased in ice cores. On Signy Island, from 1820-1880 AD a glacial advance occurred, thought to be a response to northward displacement of the Antarctic circumpolar trough (Noon *et al.* 2003). This movement of the Antarctic Circumpolar Trough correlates with the ice readvances on South Georgia at 200 <sup>14</sup>C yrs BP, reaching a maximum in 1875 AD (Birnie 1990). Peat deposits from Argentina suggest this climate deterioration also affected the Southern Ocean and Southern South America climates (Mauquoy *et al.* 2004). During the early 20<sup>th</sup> century, across the Antarctic regions glaciers advanced until 1950, when retreat began (Clapperton and Sugden 1989; Clapperton 1990; Collins 1976; Hayward 1983; Noon *et al.* 2003; Thompson 1994). This strong regional coupling during the 20<sup>th</sup> century across the Antarctic Peninsula and Sub Antarctic Islands implies a regional change in atmospheric and oceanographic circulation patterns (Noon *et al.* 2004).

## 2.3.3.5 Summary

Evidence for environmental change in the Sub Antarctic Islands and Southern Ocean through the Holocene is conflicting as a result of the spatial interactions of the Polar Front and Westerlies (Jones *et al.* 2000). Although the climate signature across the region is varied there are some significant trends documented throughout the region, implying that regional factors are influencing these changes. Data from the Palmer Deep core suggests a mid Holocene climatic optimum (hypsihermal) culminated around 3360 cal yrs BP (Domack *et al.* 2001). Records from the Antarctic Continent (Dome C) suggest a cooling followed this optimum from 2300 <sup>14</sup>C yrs BP (Masson-Delmotte *et al.* 2004) which can be correlated with the climatic deterioration at South Georgia from 2600 <sup>14</sup>C yrs BP (2600 cal yrs BP) (Rosqvist and Schuber 2003). As this pronounced cooling is documented across the Antarctic region, it suggests that a significant climate shift of regional significance occurred at this time.

Although the period of climatic deterioration is punctuated with periods of warming, there are no regional climatic trends evident in the records until approximately 1000 <sup>14</sup>C yrs BP (850 cal yrs BP), when a further cooling occurred. Evidence from the Palmer

Deep core implies that after the mid Holocene optimum, which culminated at 2600  $^{14}\text{C}$  yrs BP (2600 cal yrs BP) on South Georgia, climatic deterioration occurred, which intensified at approximately 1000  $^{14}\text{C}$  yrs BP (850 cal yrs BP), correlating with the period known as the Little Ice Age from 700 cal yrs BP to 100 cal yrs BP (Domack *et al.* 2001). Evidence suggests that the period of warming from 2000-1000  $^{14}\text{C}$  yrs BP (1850-850 cal yrs BP) is only documented at South Georgia. The forcing mechanism may be of regional origin, however, as there are a variety of regional responses to a single forcing event, it is possible that the effects on South Georgia are more pronounced than other areas of the Southern Ocean (Hall and Perry 2004). The onset of enhanced cooling began at 1400  $^{14}\text{C}$  yrs BP (1250 cal yrs BP) in the Antarctic Peninsula, 1000  $^{14}\text{C}$  yrs BP (850 cal yrs BP) on James Ross Island and 600  $^{14}\text{C}$  yrs BP on South Georgia and in the ice core record at Dome C (East Antarctica) (see figure 2.11 and 2.14). This strong coupling of the timing of climatic change in the Antarctic region suggests that the forcing mechanism is of regional or global origin (Masson-Delmotte *et al.* 2004; Ingólfsson *et al.* 1998; Björck *et al.* 1996).

The strong similarity between ocean and terrestrial records for the past 4000  $^{14}\text{C}$  years in the Antarctic Region suggests a strong coupling process is operating at this timescale (Masson-Delmotte *et al.* 2004). In all records the 2600 and 600  $^{14}\text{C}$  year BP (2600 and 540 cal yrs BP) events are clear, however, there are a number of smaller climatic changes occurring on a local level, suggesting a variety of climatic forcing mechanisms are affecting the region (Fabrès *et al.* 2000).

### 2.4 Historical records of climate change

The proxy record outlined in section 2.3 provides an indication of the climate conditions on South Georgia prior to human intervention. This can be compared to fur seal population fluctuations and therefore, used to evaluate the impact of climate change on the fur seal population. Natural climate changes must also be assessed during the time of human intervention to allow the impact of recent climate change on the fur seal population to be evaluated in comparison to the human induced changes. Although it can be argued that human intervention has influenced climate in the recent past, this cannot be quantified and for the purpose of this study, all climatic changes are regarded as natural environmental changes and human induced changes are regarded as those outlined in section 2.5.1.

There is a broad scientific consensus that the climate has warmed by 0.6 °C during the 20<sup>th</sup> century (IPCC 2001). Figure 2.16 shows the average annual temperature recorded on South Georgia from 1905. It is clear from this that there has been a significant warming trend since 1970, consistent with the Southern Ocean region and the Antarctic continent (Weimerskirch *et al.* 2003; Raper *et al.* 1983).

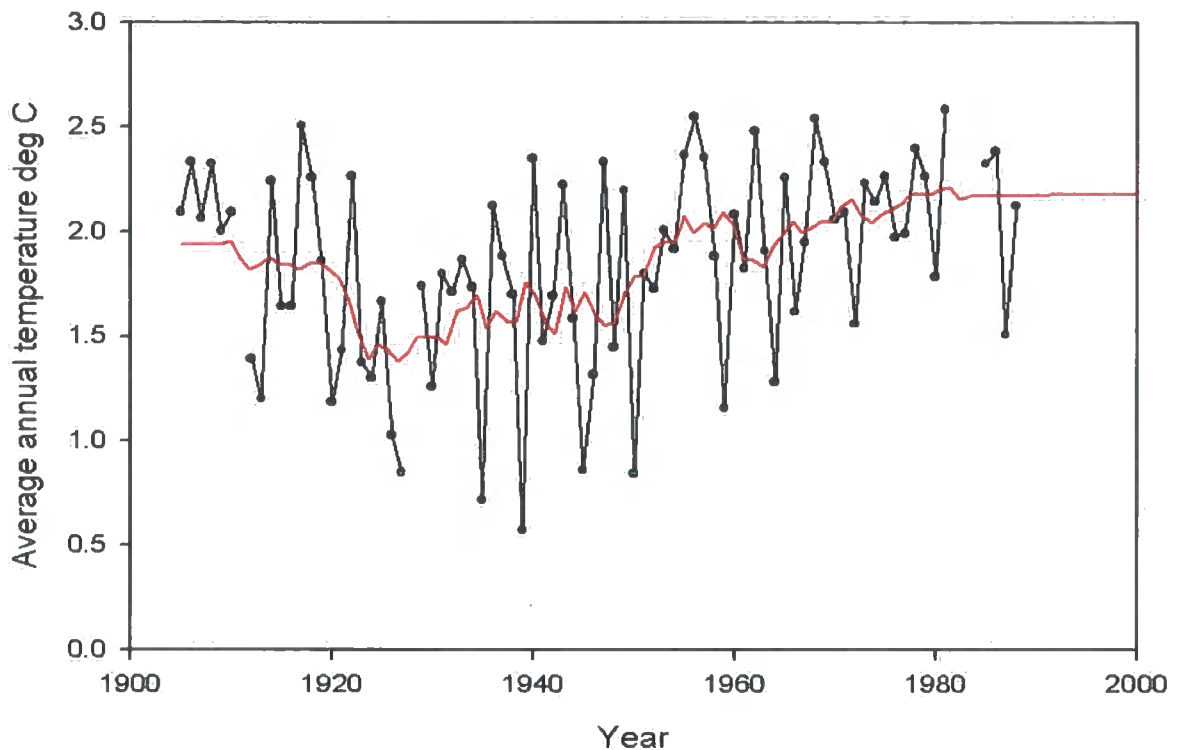


Figure 2.16: Average temperature record for Gryviken, South Georgia. The smoothed line is the running average, calculated on Sigma plot using the running average function and sampling proportion set at 0.1. Data Source: [www.antarctica.ac.uk/met/READER](http://www.antarctica.ac.uk/met/READER)

#### 2.4.1 1920-1940 (Cooling)

The coldest period during the 20<sup>th</sup> century occurred from 1923- 1939 (see figure 2.16), when annual average temperatures were up to 1.7 °C cooler than today. This is reflected in the glaciological record as glaciers reached their maximum advance during the late 1920's (Hayward 1983; Clapperton 1970). In contrast to this, Ainley *et al.* (2005) establish a warming of the sea surface temperatures from 1925-1946 as a result of a positive Pacific Decadal Oscillation (PDO). Particularly warm years are thought to be

1929/30 and 1936/7 (Whitehouse *et al.* 1996). However, as figure 2.16 shows, although 1936/37 was a warmer year within the colder period, it was still significantly cooler than the period from 1940-1960.

#### 2.4.2 1940-1960 (Warming trend)

Following this cold period, figure 2.16 highlights a warming trend from 1940-1960. During this time, McGowan *et al.* (1998) provide evidence for a strong ENSO event in 1957/58 that resulted in a warming of the oceanic temperatures, disturbing the structure of the plankton communities in the Southern Ocean and the South Pacific. This warming from the ENSO event is an anomaly within a negative PDO phase from 1947-1976, causing a decline in sea surface temperatures (Ainley *et al.* 2005). Glacier fluctuations at South Georgia during this warming phase showed a slow retreat until the late 1940's and then a short rapid advance in the early 1950's, reaching a maximum in 1956 (Hayward 1983). Variability in the glacier activity during this time reflects both the temperature regime and precipitation changes. The warming trend at South Georgia was also occurring on the Antarctic Peninsula from the 1940's and is correlated with the reduced frequency of winter sea ice since that time (Loeb *et al.* 1997).

#### 2.4.3 1960- Present day

During the 1960's and 1970's temperatures remained relatively constant at South Georgia. Figure 2.16 shows that from 1970 the temperature increased more rapidly than previously during the 20<sup>th</sup> century. This is consistent with all other terrestrial and marine records in the Southern Ocean region and suggests a regional or global forcing mechanism influenced the climate at this time (Wiemerskirch *et al.* 2003). Coupled with this increase in temperature, sea ice extent declined across the Southern Ocean region and glaciers retreated on South Georgia (Croxall *et al.* 2002; Hayward 1983). This warming is also evident from the PDO index which was strongly positive from 1977 to 1988, when two periodicities coincided, causing this to be the most intensive positive regime in the 20<sup>th</sup> century (Ainley *et al.* 2005).

From the mid 1980's, records from across the Southern Ocean region suggest the mean temperature remained constant (Wiemerskirch *et al.* 2003). However, it is not clear whether this plateau occurred on South Georgia due to the incomplete data set (see figure 2.16). The PDO index suggests a short negative (cooler) phase from 1989-91

followed by a warmer phase that has lasted from 1992 until the present day (Ainley *et al.* 2005). Although this was a warming period, it is widely recognised that strong ENSO events occurred in 1982/83 and 1997/98, causing extreme cold anomalies in the Southern Ocean in the South Georgia region, a result of the intrusion of the Southern Atlantic Circumpolar Current front (McGowan *et al.* 1998). These cold intrusions correlate with air temperature measurements on South Georgia, implying that the climate of South Georgia is very susceptible to ENSO events (Meredith *et al.* 2005).

### 2.5 Fur seal population on South Georgia

South Georgia was first explored in 1775 (after first sightings by Cook in 1675), with sealing developing rapidly in the latter part of the 18<sup>th</sup> and early 19<sup>th</sup> centuries (Headland 1982). The exploitation of fur seals commenced in 1786 therefore, the actual fur seal population prior to exploitation was never documented (Headland 1984). Due to the high competition for the seals and thus, commercial secrecy, very few sealing expeditions following the discovery of South Georgia have been documented. The number of seals taken from the island during the sealing epoch from documented expeditions is also unknown as the sealers maintained secrecy about places with a large fur seal population in the hope that they could exploit seals in subsequent seasons without any competition.

#### 2.5.1 Exploitation

There are thought to have been 3 peaks in sealing activity, the first and largest exploitation took place from 1786-1802. Records of the number of skins taken during this time are very limited, however, some records suggest that in one season (1800/01) a minimum of 112,000 skins were taken (Headland 1984). Following this first sealing epoch, the Napoleonic wars prevented any sealing occurring again until 1814. During this second sealing epoch, exploitation was not as extensive as the seal stocks of South Georgia were depleted therefore, sealers began to exploit other islands such as the South Shetland Islands which had previously not been discovered. This shift to other islands reduced the pressure on South Georgian seal stocks, which were still very low, as they had not recovered from the first period of sealing (Headland 1984). By 1822 it was calculated that 1,200,000 fur skins had been taken and the fur seal population was nearly extinct, causing the sealing to cease in 1823 (Bonner 1994). A third peak occurred again in 1869, however, as the fur seal population had been exploited so

extensively, the focus was predominantly upon the elephant and leopard seals rather than the fur seals, and very few were taken from the island (Headland 1984). Elephant seal populations did not suffer in the way fur seal populations did, as elephant seal oil was not as valuable therefore, it was only profitable to hunt elephant seals in areas where they were abundant. Fur seals however, were more valuable hence, it was profitable to take fur seals even from areas with very few seals (Headland 1982). Although the population had reached almost extinction, small-scale hunting continued until 1907, which is thought to be responsible for the halting recovery of the population during the second half of the 19<sup>th</sup> Century (Headland 1984).

### 2.5.2 Post Exploitation

Although census data has improved during the 20<sup>th</sup> century, the foraging nature of fur seals causes data collection to be problematic hence, many data sets are only estimates and there are no continuous records available (Payne 1977). Despite this lack of census data, it is widely documented that the fur seal population in the Southern Ocean increased rapidly following exploitation (Headland 1984; Hodgson *et al.* 1997; Sun *et al.* 2004; Payne 1977; Bonner 1985). Table 2.1 and figure 2.17 show the available census data at South Georgia.

| Year          | Number observed | Pup Production | Total population estimate | Rate of population increase | Location    | Source                             |
|---------------|-----------------|----------------|---------------------------|-----------------------------|-------------|------------------------------------|
| 1930          |                 | 1              |                           |                             | Bird Island | Payne (1977)                       |
| 1933          | 38              |                |                           |                             | Bird Island | Payne (1977)                       |
| 1936          | 59              | 12             |                           |                             | Bird Island | Payne (1977); Laws (1973)          |
| 1956          |                 | 3500           | 13000                     |                             |             | Bonner (1985); Boveng et al (1998) |
| 1957          |                 | 5350           | 15000                     |                             |             | Bonner (1968); Laws (1973)         |
| 1957/8-1972/3 |                 |                |                           | 16.8%                       |             | Boyd (1993)                        |
| 1958          |                 | 6800           |                           | 27.10%                      |             | Bonner (1968)                      |
| 1959          |                 | 8300           |                           | 22.10%                      |             | Bonner (1968)                      |
| 1960          |                 | 9400           |                           | 13.30%                      |             | Bonner (1968)                      |
| 1961          |                 | 9900           |                           | 5.30%                       |             | Bonner (1968)                      |
| 1962          |                 | 10200          |                           | 3%                          |             | Bonner (1968)                      |
| 1963          |                 | 11500          |                           |                             |             | Laws (1973)                        |
| 1972          | 43037           | 60000          | 150000-200000             |                             |             | Payne (1977); Laws (1973)          |
| 1972/3-1976/7 |                 |                |                           | 11.5%                       |             | Boyd (1993)                        |
| 1975          |                 | 90000          | 369000                    | 16.80%                      |             | Payne (1977); Bonner (1985)        |
| 1976          |                 | 10200          |                           |                             |             | Croxall and Prince (1979)          |
| 1976/7-1990/1 |                 |                |                           | 9.8%                        |             | Boveng et al (1998)                |
| 1982          |                 | 20900          | 856000                    |                             |             | Bonner (1985)                      |
| 1990/1        |                 | 269000         | 1500000                   |                             |             | Boyd (1993); Boveng et al (1998)   |
| 1999          |                 |                | 3000000                   |                             |             | ATCM (1999)                        |

Table 2.1: All the available fur seal population census data from South Georgia 1930-1999. Adapted from Grant, S. (pers. comm.)

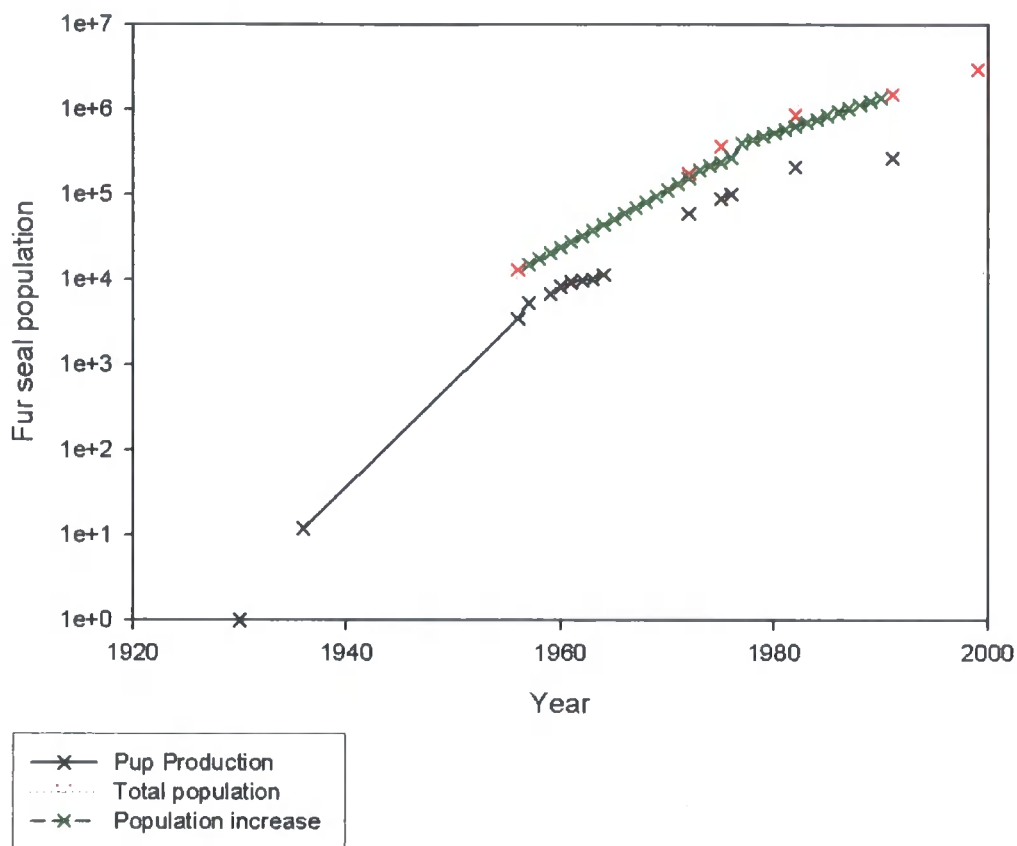


Figure 2.17: A graph showing the estimated rates of fur seal population increase at South Georgia from 1930-2000. Data is used from sources outlined in table 2.1 (note logarithmic scale for population)

The census data for mainland South Georgia and specifically the study site (Maiviken) is limited, however, the record for Bird Island is more extensive as the rapid increase in fur seals in this region caught the attention of many researchers. Table 2.1 indicates that in 1930 the first pups were born at Bird Island following the sealing industry (Bonner and Walton 1985). By 1933 the population had reached 38 seals and by 1936 this had increased to 59 (Payne 1977). From this initial census, the population documentation is very limited until 1956, when thriving colonies were observed at Bird Island and on the main island of South Georgia. On Bird Island, during the 1957/58 season, 5,350 pups were counted, increasing to 11,500 in 1963/64 and 102,000 in 1976/77 (Croxtall and Prince 1979; Laws 1973). By 1963/4 the most suitable areas on Bird Island were occupied by breeding seals, forcing nuclei of further colonies to be established on the mainland of South Georgia (Payne 1977). During 1975/76 the population on the

mainland exceeded that of Bird Island, with over half the total pups born on mainland beaches, the total fur seal population of South Georgia being estimated at 369,000 and increasing at a rate of 16.8 % per annum (Bonner 1985; Payne 1977).

Following the rapid increase in the population from the 1930's to 1970's, Croxall and Prince (1979) document reduced breeding success at Bird Island in 1977/78. This decline in the fur seal population has been correlated with a reduced krill population as a result of a change in the water currents surrounding the island (Bonner and Walton 1985). Following this brief decline in the growth rate, the 1980's saw the population stabilise and the rate of increase declined to 9.8% per annum as the population reached 856,000 in 1982 (Bonner 1985). By 1999, the total population was estimated to be 3,000,000 however, the rate of increase was declining with some years experiencing a negative growth rate (Boveng *et al.* 1998; Hucke-Gaete *et al.* 2004; ATCM 1999). Particularly significant years of decline were documented in 1991, 1994 and 1998, and were linked to ENSO events (Reid and Croxall 2001).

As the fur seal record is not continuous and most years are estimates, it is difficult to determine whether the population declined briefly in some years. Although the rate of increase has changed, the actual rate of change is difficult to determine as it is based on a few estimates hence, the precise timing of the change cannot be correlated accurately with climate changes and the short-term impacts on the fur seal population cannot be assessed.

### 2.5.3 The Situation Today

At South Georgia the fur seal population expanded rapidly from initial recolonisation on Bird Island during the early 20<sup>th</sup> century. Although the population has expanded onto the mainland today 75% of the fur seal population in the Southern Ocean still breed within a 50 km radius of Bird Island (Barlow *et al.* 2002). The rate of increase at Bird Island has declined as the carrying capacity has been attained on the island therefore; the population is forced to migrate to other areas where the point of saturation has not already been reached (Barlow *et al.* 2002). At Maiviken there is no fur seal census data, however, due to proximity to Bird Island, it can be assumed that the population formed as Bird Island reached its carrying capacity and hence, immigration of the fur seals took place. Although the population of Bird Island has stabilised, evidence suggests that

populations on all mainland coastal areas continue to increase (SCAR 1999). Observations in 2003 at Maiviken suggest fur seals are present in large numbers and are causing damage to the tussock grass (Bentley, M., pers. comm.) supporting the inference of an increasing population

### 2.6 Fur seal population of the Sub Antarctic Islands

Although South Georgia is the main breeding ground for the Antarctic Fur Seal in the Southern Ocean, the population of fur seals on other sub Antarctic islands is also increasing at a rapid rate (Hodgson *et al.* 1998; Sun *et al.* 2004). It is thought that the rapid rate of population increase on the other islands in the Southern Ocean is augmented by the immigration of fur seals from South Georgia (Hucke-Gaete *et al.* 2004). It is therefore necessary to consider the rate and timing of these population changes to evaluate the factors which may have caused this migration from South Georgia.

In 1948, the South Orkney Islands were the first islands to be recolonised by fur seals after South Georgia. From 1977 to 1994 the population increased rapidly and in 1994 the fur seal population reached 20,500 (Hodgson *et al.* 1998; Laws 1973). The South Shetland Islands were free from seal harvesting 20 years prior to South Georgia, and even though the extent of exploitation was not as great, recolonisation did not occur until 1958 (Boveng *et al.* 1998). Since then the growth rate of the main colonies has not exceeded 11% per annum. The densities of the breeding colonies are much lower on the South Shetland Islands than on South Georgia and it is unusual that the growth rate of the fur seal population is lower than on South Georgia. This suggests that population density has not been a primary factor limiting population growth rates (Boveng *et al.* 1998). Although some minor colonies on the South Shetland Islands have increased much more rapidly, with population growth rates reaching a maximum of 58%, such a rapid increase is biologically impossible from breeding alone therefore, the rapid increase is thought to be a result of immigration from South Georgia (Bonner 1985; Hucke-Gaete *et al.* 2004). After 1990, the growth rate of all the colonies on the South Shetland Islands slowed to 4.6% and the population is now 30,000 (Hucke-Gaete *et al.* 2004; Boveng *et al.* 1998). This stabilisation of the population growth rate suggests that immigration from South Georgia has ceased and the colonies on South Shetland are now self-regulatory. However, the population is of a magnitude lower than levels prior

to exploitation (Boveng *et al.* 1998). Calculating the magnitude of the South Georgia population in comparison to levels prior to exploitation will provide a key insight into the factors controlling population recovery and the impact the sealing industry has upon Antarctic ecosystems.

Other islands in the Southern Ocean, for example Marion Island and Heard Island have experienced similar growth rates to South Georgia after exploitation (Hofmeyr *et al.* 1997; Page *et al.* 2003; Guinet *et al.* 1994). The reestablishment of the fur seal population after exploitation on these other islands was delayed in comparison to the South Georgia and populations were not established until the mid 20<sup>th</sup> century (Page *et al.* 2003). Although the rate of increase was similar to South Georgia, (growth rates reached 17% on Marion Island) rates were not sustained for as long and today the populations have reached maturity and the growth rates have slowed dramatically (Hofmeyr *et al.* 1997; Guinet *et al.* 1994). From this evidence, it would appear that the South Georgia population is unique, as the high population growth rate has been maintained for a sustained period of time.

### 2.7 Possible causes for the increase in fur seals

It is widely recognised that the primary influences on population growth are the availability of prey and predator competition (Croxall and Prince 1979; Reid *et al.* 1999; Murphy and Reid 2001). As Weimerskirch *et al.* (2003) demonstrate, decline in food availability at lower trophic levels may underlie the general decline of top predator populations such as fur seals. The primary prey of the fur seal is krill (*Euphausia superba*) therefore, factors influencing the abundance and distribution of krill are key in determining the growth of the fur seal population. Long-term population studies of predators at South Georgia have shown that reductions in breeding performance occur in years of low krill abundance (McCafferty *et al.* 1999; Siegel *et al.* 1998; Croxall 1992; Reid and Croxall 2001; Clarke and Harris 2002). Although extensive studies have outlined the impact of fluctuations in prey availability in influencing fur seal populations, very little consideration has been given to the effect of predator populations (Boyd and Murray 2001; Thomson *et al.* 2000). Predator populations however, are also a potential factor which may influence population growth and should be considered when evaluating the possible causes of a step change in population growth.

Although there are a number of factors that influence population growth, ultimately these factors relate to the availability of prey and the extent of predator competition. Factors influencing the predator competition and prey availability can be categorised in two ways, firstly natural environmental changes and secondly human induced changes.

### 2.7.1 Human induced causes

Following the discovery of South Georgia in 1775, human influences have altered the dynamics of the ecosystem and consequent predator- prey relations, which have impacted on the fur seal population. The human influence on prey availability and predator competition and the effect on fur seal populations are examined below.

#### 2.7.1.1 Prey Availability

The full extent to which prey availability affects fur seal populations is unknown as the system is complex and there are a number of contributory factors. The primary human induced cause of reduced prey at South Georgia is thought to be the whaling industry.

As discussed in section 1.4.2.2, South Georgia was the principal centre for whaling in the Southern Hemisphere and this extensive whaling caused a reduction in whales and resulted in a krill surplus and allowing a greater fur seal population to be supported (Croxall 1992). Although this had an impact on other populations in the Southern Ocean, for example gentoo and chinstrap penguins (Croll and Tershy 1998; Croxall *et al.* 1981), fur seals are the third most important consumers of krill, and so the impact upon the fur seal population was greater than the impact on these other species. The krill surplus is now widely recognised as the most probable cause of the increase in fur seals (Doidge and Croxall 1985; Croxall and Prince 1979; Croxall 1992; Green *et al.* 1989). This is for several reasons as Croxall (1992) indicates; firstly, the removal of the Baleen whale reduced competition for krill within the Southern Ocean is the most significant short-term perturbation the Southern Ocean has ever sustained. Secondly, although krill populations are vast, their distribution is patchy and hence, will sustain long-term increases in predators before limiting populations. In areas of high-krill abundance, recovery rates and reproductive performance of species are faster and better than elsewhere.

### 2.7.1.2 Predator Competition

The primary human influence on the predator competition for the fur seal is the act of killing the fur seal. The ending of the sealing industry and the implementation of rational conservation measures made it illegal to kill fur seals without a permit (Headland 1982). This reduced the number of fur seal predators (humans) therefore, allowing the population to recover (Lewis-Smith 1988).

### 2.7.2 Summary of human induced factors

It is clear that the sealing and whaling industries had a significant effect on the fur seal population, with changes in prey availability being the most influential factor controlling populations. For example, southern elephant seals were also exploited at South Georgia at the end of the 19<sup>th</sup> century and the population is now stable at 300,000 (Headland 1984). The difference between these two species is their prey; fur seal prey is predominantly krill, however, elephant seals feed predominately on squid and hence, did not directly benefit from the krill surplus created as a result of the whaling industry. Although prey availability was affected by human induced changes (i.e. the sealing and whaling industries), natural environmental changes can also have a significant impact on krill availability and predator populations (Reid and Arnould 1996).

### 2.7.3 Natural Environmental changes

Natural environmental changes are often operating at a similar time to human induced changes, however, as human-induced changes are often more apparent, these natural changes are often difficult to establish or even ignored. These natural changes must also be considered to evaluate how the fur seal population responded to changes prior to human intervention, allowing the impact of human induced changes on the fur seal population to be assessed. I shall now briefly examine these various natural aspects of fur seal population fluctuations.

#### 2.7.3.1 Prey Availability

Although there is strong evidence in support of the krill surplus hypothesis, Reid and Arnould (1996) indicate that the distribution and abundance of krill is likely to be

dependent on a number of oceanographic and biological characteristics, changing in response to natural climate changes, thus, demonstrating the difficulty of attempting to establish a single causal mechanism for the change.

### 2.7.3.1.1 Climate

As Weimerskirch *et al.* (2003) highlight, correlations of large-scale climate changes and population sizes worldwide relate to abiotic components such as sea ice extent, sea surface temperatures and air temperature anomalies. As these factors affect the extent of an ecological niche, it would appear that climate change is a prime factor affecting the ecosystems (Meredith *et al.* 2005). Ainley *et al.* (2005) indicate in the Southern Ocean, ocean circulation and temperature is affected by Pacific Decadal Oscillation (PDO) and to some extent North Atlantic Oscillation (NAO). These anomalies in the Southern Ocean can cause changes in pressure systems and wind regimes that in turn affect ocean processes. Although this can directly affect populations through determining the temperature and hence, the ecological niche, indirectly it can also affect the population through influencing prey availability and hence, affecting the competition for prey.

As Croxall (1992) finds, years of major unavailability of krill correlate with major ENSO events. Studies suggest that although a reduction does not influence the adult population, ENSO years correlate with a significantly lower fur seal pup production (Guinet *et al.* 1994). ENSO events alter the ocean circulation and as the Antarctic Circumpolar Current (ACC) is the primary mechanism transporting krill to South Georgia any fluctuation in the ACC will have a major influence on the reproductive success of the fur seal and other krill-dependent predators (Clarke and Harris 2002). The link between prey availability and ENSO events implies climatic change indirectly affects the fur seal population and it can be argued that the increase in the fur seal population correlates with recent 20<sup>th</sup> century warming.

Regional warming on the Antarctic Peninsula within the last 50 years has had a significant impact on the sea ice extent and it is now widely recognised that changes in populations are correlated to changes in sea ice extent (Ainley *et al.* 2005; Curran *et al.* 2003 Clarke and Harris 2002; Croxall *et al.* 2002). For example, as McCafferty *et al.* (1999) suggest, adélie penguins are inversely related to winter sea ice at Ross Island, and hence, have increased in the past 40 years as the sea ice during this time has declined. Alternatively Emperor penguins populations have declined over the past 50

years, suggesting a positive relationship with the sea ice conditions. Although few studies suggest that fur seals are affected directly by ice, populations may be affected indirectly if ice cover influences the prey populations and competition from other predators or predation (Croxall 1992; Croxall and Nicol 2004). It is widely recognised that krill reproduction and survival are significantly affected by the extent and duration of ice cover and as Loeb *et al.* (1997) highlight, since the 1980's regional warming associated with reduced sea ice extent has reduced the krill abundance, thereby diminishing the prey available for fur seal populations (Smetacek *et al.* 1990; Reid and Croxall 2001).

### 2.7.3.1.2 Competition

Barlow *et al.* (2002) established that years of the lowest reproductive output by predators at South Georgia have become more frequent in the last decade. Competition for krill is increasing and populations are having more difficulty surviving in years of low krill abundance. As Reid and Croxall (2001) suggest, the period of krill surplus following the whaling industry has now ended at South Georgia and due to the decline in krill there is now increased competition for prey between top predators. As Boyd and Murray (2001) highlight, krill is the dominant constituent in the diet of fur seals, gentoo penguins and macaroni penguins therefore, a change in any of these populations is likely to impact upon the krill population and hence, indirectly affect the fur seal population.

Extensive research has shown that other species such as Adélie penguins, gentoo penguins, fulmars and snow petrels have been affected by climate change during the 20<sup>th</sup> century (Croxall *et al.* 2002). For example, Thompson *et al.* (2001) highlight that fulmar populations have expanded in the past two centuries as a result of the oceanographic changes taking place. These changes in population increase the competition for krill in the Southern Ocean and therefore, reduce the population of fur seals that can be sustained.

By contrast Barlow *et al.* (2002) suggest that increased competition does not affect the fur seal population as significantly as other populations. The decline in the krill population of the Southern Ocean does not appear to have significantly affected the fur seal population, however, the macaroni penguin population (also a krill predator) are reduced. Barlow *et al.* (2002) suggest this may be due to the competitive advantage fur

seals have over other krill predator populations. If this is the case, as Scheffer *et al.* (2001) highlight, it is increasingly clear that competition and predation are much more important in driving oceanic community dynamics than previously thought.

### 2.7.3.1.3 Summary of prey availability

It appears that although fur seals are significantly affected by prey availability, this is not in response to increased competition for prey. In studies of the competition between fur seals and other species (macaroni penguins), the exploitation of krill favours fur seals (Barlow *et al.* 2002; Croll and Tershy 1998). Hence, a decline in fur seal prey availability is not a result of increased competition from other predators but from large-scale environmental changes. Although if the fur seal population continues to increase, and the krill population continues to decline, it is likely that small scale fluctuations in krill populations are more likely to affect the fur seal population dynamics.

### 2.7.3.2 Predator competition

As fur seals are top predators very few studies have analysed the effect of predator populations on the fur seals, however, as a study by Boveng *et al.* (1998) highlighted, predator populations can dramatically affect fur seal populations and this factor must be taken into consideration when analysing past populations and possible influences on population growth. An increase in predators, as a result of natural environmental changes may have a negative effect on the fur seal population if fur seals are prey for these species. The main predator of the fur seal is the leopard seal, whose distribution is affected by sea ice and terrain (Boveng *et al.* 1998)

#### 2.7.3.2.1 Sea Ice

Boveng *et al.*'s (1998) study established that the fur seal population growth on the South Shetland Islands is influenced by leopard seal predation. Yet this does not appear to be the case at South Georgia as leopard seals are absent during the fur seal breeding season. As leopard seals abundance increases with proximity to sea ice, (sea ice is within 200km of the South Shetland Islands during the fur seal breeding season, in comparison to within 800km of South Georgia) this appears to be an influential factor (see figure 2.18) (Boveng *et al.* 1998). Although leopard seals do not appear to influence the fur seal population on South Georgia today, during the late Holocene, it is possible that sea ice extent was more extensive therefore, the leopard seals may be

within a closer proximity to the fur seals at South Georgia, having a negative impact on the population as observed at the South Shetland Islands today.

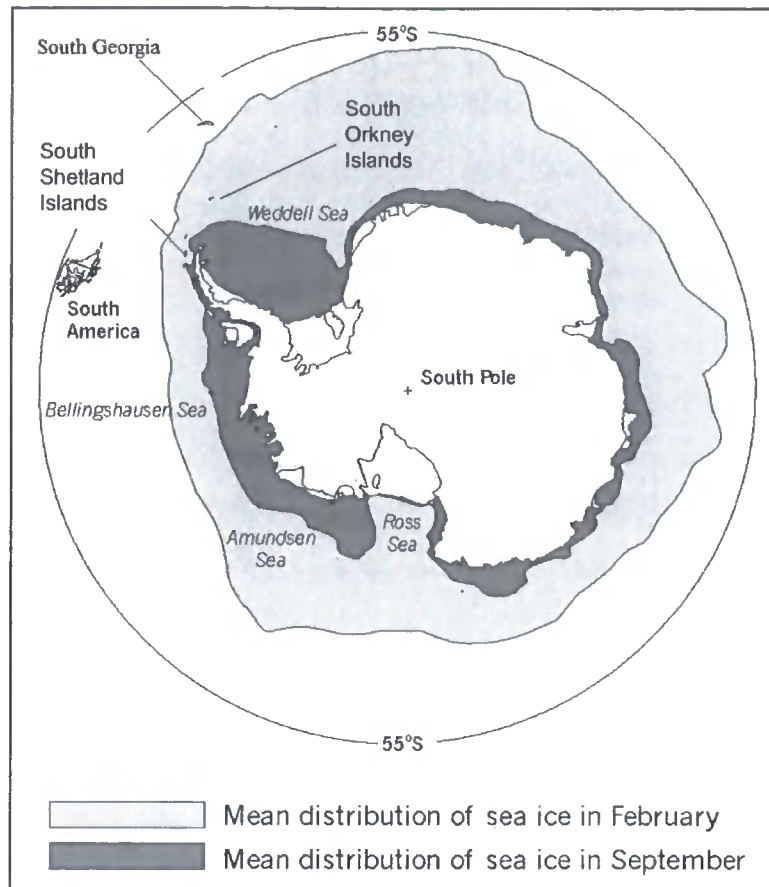


Figure 2.18: Mean sea ice distribution in the Antarctic region. Source: Hansom and Gordon (1998)

#### 2.7.3.2.2 Terrain

The terrain of the fur seal breeding sites on the South Shetland Islands is also influential in increasing the impact of the leopard seal on the fur seal population. On the South Shetland Islands, breeding sites are backed by steep rocky slopes or gentle slopes that are more exposed to other species therefore, the fur seals do not spend as much time on the shore as on South Georgia hence, are more exposed to predation by the leopard seal (Boveng *et al.* 1998). Climate changes such as glacial advance and retreat may have altered the environment of South Georgia, consequently fur seal breeding sites were not as favourable as today, forcing the fur seals into the ocean for longer periods and increasing the threat of predation. Although as discussed in section 2.3.2.1, the

Maiviken area has not been glaciated since the LGM hence, this factor is unlikely to have affected the fur seal population in the late Holocene.

### 2.7.3.2.3 Summary of predator competition

Although the affect of predator competition does not appear to be an issue at South Georgia today, as Boveng *et al.* (1998) indicate, if environmental factors are favourable to leopard seals this can negatively affect the fur seal population. Historically, the situation at South Georgia has changed and as a result it is possible that during the Holocene the environment of South Georgia has altered, making it more favourable to other species that were potentially fur seal predators.

### 2.4.1 Summary of natural environmental changes

It is widely accepted that climate change has a profound affect upon biotic components of marine ecosystems, however, the direct impact upon the fur seal population is unclear and the role of climatic variation in regulating marine populations and communities is not well understood (McGowan *et al.* 1998; Weimerskirch *et al.* 2003; Croxall and Nicol 2004). This is due to a number of reasons; firstly interpreting the biological response to climate change is complicated by the highly coupled nature of the atmosphere-ice-ocean systems of the Southern Ocean; making it difficult to determine the cause of such changes (Croxall *et al.* 2002). Secondly, as breeding performance integrates measures of predator and prey behaviour over relatively long time periods both predator and prey may respond to a number of interlinked environmental factors, generating difficulties associated in defining the primary cause of change in either predator or prey populations (McCafferty *et al.* 1999). Thirdly, the biological consequences of climatic variability of the atmosphere and ocean are largely unknown (McGowan *et al.* 1998). Despite these uncertainties, research has highlighted that marine populations do respond to climatic events and major changes have taken place in the marine ecosystems in the past twenty years (McGowan *et al.* 1998).

### 2.7.4 Summary of factors affects fur seal populations

Evidence suggests that the primary forcing factor influencing the fur seal population today is the availability of Antarctic krill. Although the abundance of krill is intimately linked to climate variability, it has also been influenced by human induced causes. To

determine the individual impact of these differing causes, it is necessary to obtain long-term data sets extending back prior to human intervention.

The possible long-term impacts of the growth in fur seal populations can only be fully comprehended from an appreciation of the natural change in fur seal populations and its response to environmental change (Ellis-Evans 1990). However, due to the rapid increase in fur seal populations during the 20<sup>th</sup> century, smaller, annual fluctuations in population cannot be identified and related to environmental change. Reconstructing Antarctic fur seal populations through the Holocene will allow an assessment of fur seal population fluctuations prior to human intervention and provide longer-term context within which to assess recent changes. This will then help to determine the extent human induced changes have had on the population, aiding management decisions.

### 2.8 Fur seals on South Georgia and their impacts

One of the key reasons to determine the cause of the fur seal population increase at South Georgia is to evaluate the controlling factors underlying the fur seal population fluctuations to aid management and conservation decisions. To fully determine the potential affect future fur seal population growth may have on the environment, the current effects of the fur seal population on the natural environment must be first evaluated. This section will evaluate the impact the increasing fur seal population is having on the environment at South Georgia.

Today the rapid increase in fur seals is altering the natural environment of South Georgia and threatening the existence of many bird and plant species. Although this impact is thought to be significant, the full impact of the fur seals on the terrestrial and freshwater systems at South Georgia has not been fully assessed. However, on Signy Island, where population recovery began approximately 20 years earlier than South Georgia, the impact has been determined and it is thought that the fur seals are causing irreversible damage to the environment (Lewis-Smith 1988). Although the rate of recovery at Signy Island was more rapid than on South Georgia, today the fur seal populations are at similar levels on both islands.

The primary vegetation in South Georgia is tussock grass (*poa flabellata*), occurring on raised beaches and other lowland areas (see figure 2.10). This tussock grass is the main

breeding ground for the fur seals, however, it is being dramatically altered by their increase (Headland 1984). As the tussock grass is a major habitat for fur seals, their excreta enrich the soil, producing deep green luxuriant growth of grass. This increased growth of tussock grass increases the size and abundance of leaves, shading surrounding plants and consequently reducing their growth (Bonner 1985; Headland 1984). Although growth of the tussock has increased in areas abundant in fur seals, the tussock grass is being rapidly eroded. Fur seals lie on the crown of the tussock crushing leaves and shoots, if this is only temporary the tussock grass recovers. The increased population however, is creating an increased pressure on the tussock grass and the tussocks do not have time to recover as the fur seals repeatedly lie on the tussocks, resulting in bare peaty mounds that may be colonised by algae (Bonner 1985). Seals moving across the tussocks further erode the vegetation and the soil between the plants, forming pedestals of vegetation (see figure 2.19) (Headland 1984). This destroys the habitats of many invertebrates such as permylopid beetles, coleopeta, diptera, collembola and acarina to such an extent that these species are now facing extinction (Bonner 1985).



Figure 2.19: Fur seals sitting in tussock grass, illustrating the primary vegetation of South Georgia (tussock grass).



Figure 2.20: A fur seal lying on a mound of tussock grass while feeding her pup. As the population increases, the tussocks are occupied by fur seals for longer periods, not allowing the tussock grass to recover. Source: Bonner (1994:57)

As Croxall *et al.* (1990) document, other larger species are also threatened as a result of the declining tussock grass. In the areas with most abundant seals, albatross breeding has declined; this is thought to be because the fur seals have destroyed the albatross' breeding habitat (tussock grass) depriving the birds of breeding and exposing them to predation (Bonner 1985). Although there is no evidence that seals are adversely affecting breeding success or survival, the proportion of birds being recruited into a breeding population are avoiding areas where seals are abundant and breeding in areas where fur seals are absent. On Signy Island several giant petrel colonies have also been abandoned due to fur seal disturbance (Lewis-Smith 1990).

In several localities, extensive areas of moss carpet bog have been compacted and recolonised by nitrophilous alga and in some areas this erosion has been so extensive that all vegetation has been destroyed, leaving large areas of bare soil to be colonised by *Prasida crispa* and other resilient algae (Headland 1984). This movement of seals and the consequent destruction of vegetation have caused major peat and soil erosion as the reduction in vegetation cover is exposing the soil, increasing the amount washed away in surface run off. Removal of the soil in this manner is also disrupting loosely attached mosses and lichens. Such erosion is increased further in areas where seals occupy the

tussocks as the water table is at or near the surface, pools of stagnant water form between the tussocks, further increasing the erosion of the tussock grass (see figure 2.21) (Lewis-Smith 1981).



Figure 2.21: Fur seals lying on tussock grass. As a result pools of mud have developed among the tussocks and increasing erosion.

In addition to its erosion, the remaining soil is becoming more acidic and higher in nitrogen levels as seal excrement alters the chemistry of the soil. Although this has acted as a fertiliser, this has also had negative effects on the fresh water environments; causing eutrophication, leading to the domination by few taxa and modifying the microbiota of the freshwater system (Hawes 1990; Lewis- Smith 1990).

As the fur seal population increases, the population is expanding from its initial breeding ground on Bird Island and the fur seals are migrating to the coastal areas on the mainland of South Georgia. Although the greatest impact is on the passage of the fur seals as they move from the sea to inland resting sites, population expansion means that coastal regions are overpopulated, causing the fur seals to migrate further and further inland, expanding the impact of fur seals. As a result of this, today slopes up to almost 200 metres altitude are now being threatened (see figure 2.22) (Croxall and Prince 1979; Bonner 1985; Lewis-Smith 1988). This is now causing extensive changes to terrestrial and freshwater systems and in some areas damaging Antarctic Specially Protected Areas (ASPAs) as the composition of communities is being drastically altered (Hodgson *et al.* 1998; Lewis-Smith 1990). It is estimated that fur seal induced changes on Signy

Island are the greatest and most rapid since the retreat of the Pleistocene ice sheet (Lewis-Smith 1990).



Figure 2.22: Fur seals on the beaches of Maiviken. The vegetated slopes behind the beach are now being eroded as the fur seal population increases.

### 2.8.1 Management of fur seals on South Georgia

The sub Antarctic ecosystem is a fragile environment and recovery of this environment is slow even to minor damage (Headland 1984). Destruction of the environment poses important questions for conservationists and environmentalists (Lewis-Smith 1988). Firstly should seals remain a specially protected species in accordance with Antarctic Treaty Agreed Measures on the Conservation of Antarctic flora and fauna to permit numbers to increase and establish a breeding population, while destroying unique terrestrial and freshwater environments? Alternatively, should fur seal population growth be restricted through reducing these measures whilst protecting the environment through a series of control measures? Fur seals were initially protected due to the near extinction of the species as a consequence of the rapid human exploitation. As this measure has been successful (perhaps *too* successful), should these protection measures be lifted to allow the environment to recover and reduce the dominance of fur seals? For example as Lewis-Smith (1988) outlines, on Bird Island, South Georgia enclosures have been formed using electrified fencing to prevent the advancement of fur seals. This has allowed substantial colonisation by green filamentous algae and encouraged the regrowth of the eroded tussock grass. If the fur seal population continues to grow at the

same rate, it is possible this population's impact is likely to have a catastrophic and irreversible affect on these systems.

The key to answering this dilemma, as Abbott and Benninghoff (1990) outline, is to determine the range of natural variability in the Antarctic ecosystem and to distinguish changes from human perturbations. This can only be comprehended from an appreciation of the natural change in fur seal populations and its response to environmental change (Ellis-Evans 1990). The increase may be a naturally occurring fluctuation, cycle or unidirectional process, however, it may be a change in response to artificial influences such as pollution or commercial harvesting (Croxall and Prince 1979). If this increase in fur seals is a result of natural causes and a similar event has happened previously, then it is likely that the fur seal populations will regulate naturally and the system will recover and restore its equilibrium and management will not be necessary. However, if this is not the case and fur seal populations in the 20<sup>th</sup> century exceed all historical populations, the likelihood that the equilibrium will be restored is lower hence, necessitating management measures to prevent the loss of unique and fragile environments.

As Croxall (1992) establishes, assessing the effects in relation to natural variability and human induced changes is difficult for a number of reasons. Firstly, the fossil record is limited, and gives few clues to the history of the species in relation to the varying environments that have characterised the Antarctic. Secondly, all documented population changes relate to human exploitation therefore, any influence of natural causes and recovery of the ecosystem cannot be assessed. Thirdly, an important gap in the knowledge is an understanding of how the physical environment influences the distribution and abundance of prey, which in turn may affect the population (Croxall *et al.* 1990). In addition to this, fur seals have low reproductive and mortality rates, thus, responses to such environmental change are slow and often hard to detect (Croxall 1992). Lastly, there are few detailed understandings of the mechanisms by which the Southern Ocean top predator populations are regulated although some plausible hypotheses are now emerging for a regulation by prey availability (Reid and Arnould 1996, Boveng *et al.* 1998). As Croxall *et al.* (2002) indicate, evidence is still-limited and these processes operating within system are only one part of the picture and other processes triggered by mechanisms outside the system may be crucial to this understanding.

## 2.9 Summary

This chapter outlines the background to the fur seal population changes and the climate changes through the Late Holocene. This background knowledge will then be applied to the results that are presented in chapter 4. The next chapter will outline the methodology for reconstructing the fur seal population through the late Holocene.

## Chapter 3

### Methodology



Plate 3: Fur seal hair after preparation.

### 3: Methodology

The use of palaeolimnology to reconstruct fur seal populations is a relatively recent development that has not been widely utilised and methodologies utilising this technique are still developing. As stated in the objectives (chapter 1), this study uses the methods outlined by Hodgson *et al.* (1998) to reconstruct the fur seal population from hair abundance in sediment cores however, due to the nature of the sediment at this site, I refined the methodology to suit the study site accordingly. Following this is geochemical analysis which is based upon techniques employed by Sun *et al.* (2004a), with alterations being made to suit the study site and the techniques available.

#### 3.1 Sediment cores

The relative depths of the cores are shown in figure 3.1. HUM3 was extracted using a Piston Corer to get the deeper sediment record, while MIAV/K was extracted using a Kullenberg corer hence, ensuring the sediment water interface was intact. Cores were transported stored in tightly sealed plastic tubing and kept cool for transportation to the UK before being stored in a cold store.

##### 3.1.1 Core depth and scaling

As figure 3.1 shows, the MAIV/K core extracted the top 90 cm of sediment. However, during transportation and storage the core shrank due to the large volume of water present in the core during extraction. For this reason when the core was sub sampled in the UK it was only 68 cm long. HUM3 core was taken 100cm below the surface of the sediment to provide a deeper record and to continue the record taken from the MAIV/K core. This core shrank by 10cm, as the volume of water in the core was not as great as MAIV/K due to the depth of the core.

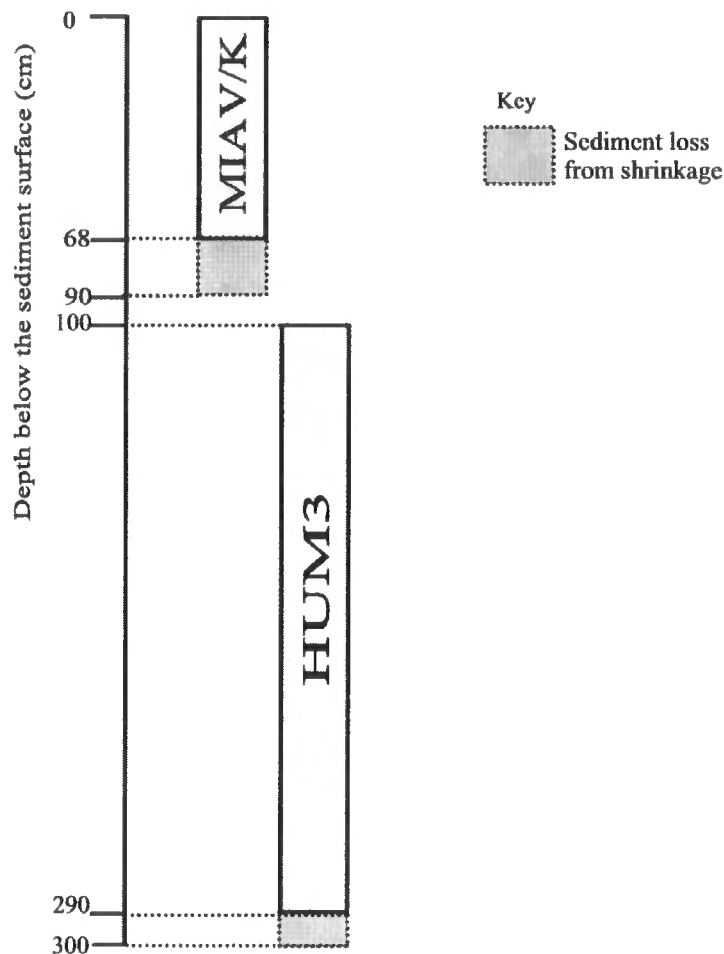


Figure 3.1: Relative depths of the cores

The shrinkage of the cores left a gap of 32cm between cores. However, as the MAIV/K core was extracted to a depth of 90cm, the actual amount of sediment not extracted is only 10cm, (90-100cm below the surface of the sediment). As in both the cores, the whole core shrank, it is unclear exactly where most of the shrinkage took place. In my methodology I refer to samples, these are the sub samples of the core and the deepest sub sample in the MAIV/K core is MAIV/K 67-68cm. However, in the results section, the depth of the total sediment extracted is referred to rather than the sub samples. As MAIV/K core actually represents the top 90cm of the lake sediment, I have expanded the depth scale to cover a total of 90cm (see equation 3.1) therefore, sub sample MAIV/K 67-68cm represents a depth of 90cm in the lake.

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Depth in the whole core = Sub sample depth x (90/68)

Equation 3.1

Calculating the depth of the sub samples in the whole core. As 90cm is the depth within the lake the core covers, however, 68cm is the actual length of sample left over after shrinkage.

### 3.1.2 Sedimentological and Stratigraphic core analysis

After extracting the core, prior to subsampling, the sedimentology of the core was analysed using the Troels- Smith criteria. This provided a broad understanding of the sedimentological changes within the core prior to analysis.

### 3.1.3 Sub sampling

To provide a means of correlation, seal hair counts and geochemical analysis were carried out at the same depths. Analysis was carried out at 8cm intervals throughout the core and as time allowed this was increased to a 4cm resolution. A finer resolution of 2cm sampling was carried out at the top of the MAIVI/K core to reconstruct the population using the proxy technique to compare with historical fur seal population records. This was specifically so that I could compare the accuracy of the proxy population to census data and hence, lead to more robust estimates of the actual populations through the Holocene, when the census data was not available.

## 3.2 Fur seal hair abundance

Hodgson *et al.* (1998) outline a method to reconstruct fur seal populations using fur seal hairs preserved in lake sediments. Fur seals have an abundance of insulating secondary hairs, which are lost during moulting and deposited in terrestrial and aquatic environments visited by the fur seals hence, incorporated into the lake sediments. The hairs remain well preserved in the lake sediments and as Hodgson and Johnston (1997) establish, a variation in seal hair number in lake sediments can indicate fluctuations in visiting seal populations; with more abundant seal hairs reflecting a larger visiting seal population (see figure 3.2).

Fur seal hair abundance can be used as a proxy from which relative fur seal populations, however, due to the complex differences in sediment input and output mechanisms between lakes, this technique cannot be used to quantify the fur seal population which could be compared to other data sets, however, it does provide an indication of the relative size of the fur seal population through time.

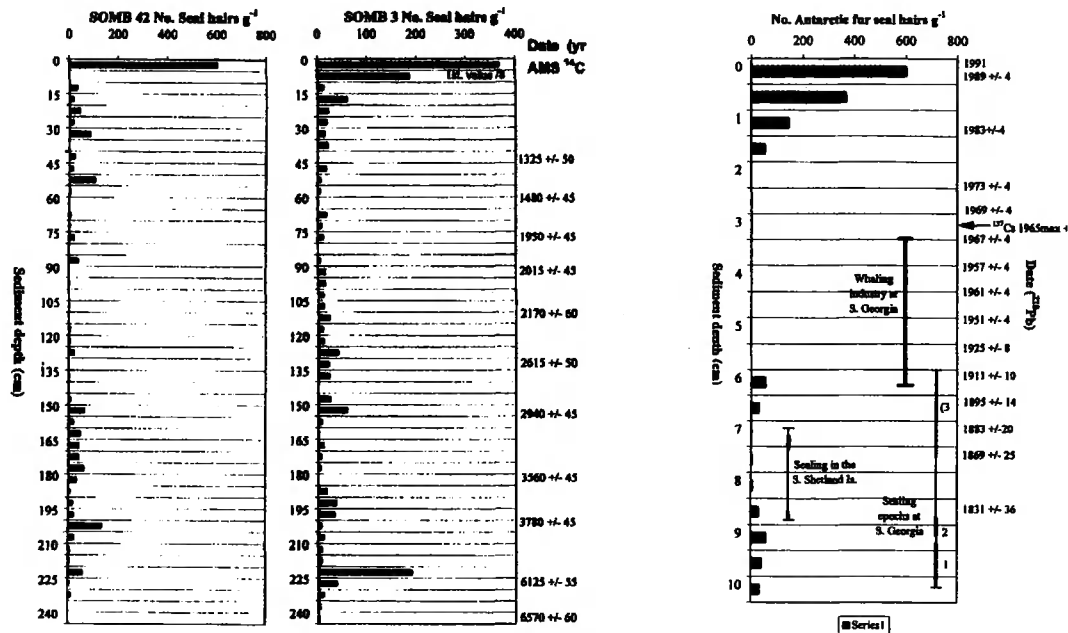


Figure 3.2: Fur seal hair abundance record from Signy Island. Source: Hodgson *et al.* (1998).

Hodgson *et al.*'s (1998) method suggested taking a known dry weight of sample and wet sieving the sediment through a 125 $\mu$ m sieve. Hair abundance was then expressed as number of hairs per 1 gram of dry weight. A test of this methodology on several samples at different intervals throughout the core did not prove successful for the sediment from Maiviken for a number of reasons. Firstly, hairs were difficult to identify and extract from the sediment due to the large amount of organic material, specifically tussock grass fragments in the samples and secondly, a number of hairs were washed through the sieve. Tests showed the proportion of hairs washed through was not consistent throughout the core due to the different organic-minerogenic composition throughout the core. To reduce this error, I tested a number of alternative techniques before deciding upon a final methodology. To allow the hair abundance to be expressed as number of hairs per 1 gram of dry weight, before any method was executed, samples were freeze-dried. Samples were frozen at -80°C, for 48 hours before being placed in a

freeze drier with a vacuum of 1.030 for 16 hours. Samples were then weighed and stored in a dessicator before being used.

### 3.3 Development and refinement of the Hodgson *et al.* (1998) technique

As the method outlined by Hodgson *et al.* (1998) was unsuitable for the sediment at Maiviken, I adapted the technique to make the counting more accurate.

#### 3.3.1 Final methodology

Before outlining the different methodologies I tested, below is a summary of the final method used for fur seal hair extraction, refined from Hodgson *et al.* (1998):

1. Samples freeze dried and weighed. (Approximately 0.3-0.4 grams (dry weight) of sediment).
2. Add 20ml of 20% hydrogen peroxide and put in a water bath for 2 hours.
3. Wash the residue back into the solution and add 45 ml of distilled water and 5 ml of ethanol.
4. Centrifuge for 10 minutes at 4000 rpm, pour off excess water and add more distilled water.
5. Sieve sample through 15 $\mu$ m, keeping the coarse material
6. Allow the sediment to settle and pour off the excess liquid.

Before finalising this methodology, I tried a number of different methods to separate the hairs from the organic matter.

#### 3.3.2 Physical separation

##### 3.3.2.1 Sieving

Sieving the sediment through a variety of different sized sieves, larger than 125 $\mu$ m (710 $\mu$ m and 1mm), allowed the hairs to pass through the sieve hence, partly separating the hairs from the coarser organic material. The hairs were found in both the coarse and fine sediment and the percentage of organic material relative to the number of hairs was not consistent in all samples. This was due to the differing sediment composition of

samples throughout the core; in organic samples more hairs were present in the coarse sample as the organic fragments trapped the hairs. In a second test that aimed to remove all the minerogenic matter, a finer sieve (63µm) was used however, the same problem occurred.

### 3.3.2.2 Particle shape analysis

A particle shape analyser was used to see if the hairs could be identified and counted, therefore, reducing the problems in identifying and extracting the hairs and providing a quick method for identifying the hairs, whilst guaranteeing that all hairs were accounted for. However, this method proved problematic as the hairs were a similar shape to wood and moss fibres making it difficult to distinguish between the two.

### 3.3.3 Chemical separation

#### 3.3.3.1 Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

Hydrogen peroxide is routinely used in diatom and pollen preparation to reduce the organic material in samples (Birnle 1990). In this study H<sub>2</sub>O<sub>2</sub> digestion was tested to see if it would separate hairs from organic (vegetation) matter. This allowed the hairs to be more visible and reduced the problems of hair being incorporated in the organics. As Marshall (1998) states, seal hair contains keratin, as does human hair therefore, to ensure seal hair would not be destroyed with the strength of the hydrogen peroxide used in diatom and pollen preparation, different strengths were tested on human hair (see table 3.1). The tests showed that H<sub>2</sub>O<sub>2</sub> only affects the colour of the hair and does not significantly affect the structure of the hair. It was inferred from this that fur seal hairs would react in a similar manner and therefore, H<sub>2</sub>O<sub>2</sub> was used on the sediment to reduce the organic material in the sediment and hence, aid in identifying the hairs.

Samples from the core were placed in 20% hydrogen peroxide and left in a water bath for 2 hours. A large amount of debris accumulated around the top of the sampling tube and the amount varied depending upon the position in the core. Extracting some of the material I identified fur seal hairs therefore, this residue was washed back into the sample. Distilled water was added and the sample was centrifuged at 4000 rpm for 10 minutes. After checking there were only occasional very small *fragments* of hair in the top of the sample, the excess water was poured off and the sample was examined.

Additional distilled water was added to the sample to dilute the solution hence, allowing the hairs to be more easily identified.

| Time/ Concentration | 20%   | 10%  | 5%                           |
|---------------------|---|--|------------------------------|
| 30 minutes          | The hair structure appeared the same, however the colour was lighter. | Hair was not destroyed, it had just lightened, but not to the extent as 20% concentration. | As 10%, but remained darker. |
| 1 hour              | Hair appeared lighter, however the structure was the same.            | ←  | Lightened.                   |
| 2 hours             | As 1 hour but lighter.  | ←  | Lightened.                   |
| 3 hours             | As 2 hours but lighter.   | ←  | Lightened                    |

Table 3.1: Results of tests of varying H<sub>2</sub>O<sub>2</sub> strengths on human hair

### 3.3.3.2 Fine Sieving

To reduce the H<sub>2</sub>O<sub>2</sub> residue and allow the hairs to be more visible without increasing the amount of water in each sample, the sample was sieved through a 15 µm sieve to see if the hairs would be retained and the cloudiness of the water reduced. Almost all the hairs were trapped in the coarse material of the sieve. Occasional fine particles of hair were in the fine section, however, these were all *fragments* of hair. As the organic material was reduced from the H<sub>2</sub>O<sub>2</sub> the proportion of hair trapped in the sieve was the same throughout the core hence, reducing the previous problems of differential effects incurred during sieving. Sieving the sample also reduced its cloudiness making identification of the hair easier. Although sieving the sediment diluted each sample significantly, once the sample had been left to stand overnight, the hairs settled and the excess solution was poured away.

### 3.3.4 Identifying hairs

Fur seals have a dual layer of hair consisting of longer coarse guard hairs overlying a layer of shorter, finer underhair (Bonner 1968) (see figure 3.3). Hodgson *et al.* (1998) found that the hair incorporated into the sediment is primarily the underfur as it is in greater abundance than guard hairs on the fur seal (ratio of 40:1). Primary hairs are

more likely to be transported through the lake without being incorporated into the sediment therefore, the underfurs are more representative of the actual fur seal population. Following the Hodgson *et al.* (1998) method, the finer underfur was counted and coarser guard hairs were ignored. The hairs were identified using the taxonomically distinct criteria listed in Scheffer (1964) and Bonner (1968). The criteria states the underfur is approximately  $15\mu - 20\mu\text{m}$  in diameter and reaches a maximum length of 2cm and individually the hairs are slightly waved (Scheffer 1964; Bonner 1968). The guard hairs are significantly longer (approximately 60mm) and coarser ( $125\text{-}150\mu\text{m}$  in diameter) and therefore, easily identified (see figure 3.3) (Bonner 1981).



Figure 3.3: Cross section of the fur layers of an Antarctic fur seal. Source: Bonner (1994:23)

### 3.1.1 Counting

A black picking tray as used in foraminiferal analysis was used to count the hairs. This allowed the hairs to be identified, as the  $\text{H}_2\text{O}_2$ -bleached hair was obvious against the black background and grid squares on the tray allowed easy counting (see figures 3.4 and 3.5). A small brush was used to move the hairs around to aid counting and hairs were identified using the criteria outlined above. Following Hodgson *et al.* (1998), all counts were expressed relative to 1-gram dry weight of sediment; calculated using equation 3.2.

$$\text{Normalised number of hairs} = \text{Total count} \times (1/\text{dry weight})$$

Equation 3.2

Calculating the normalised number of hairs per 1g of dry weight from raw counts of a known weight of sediment.

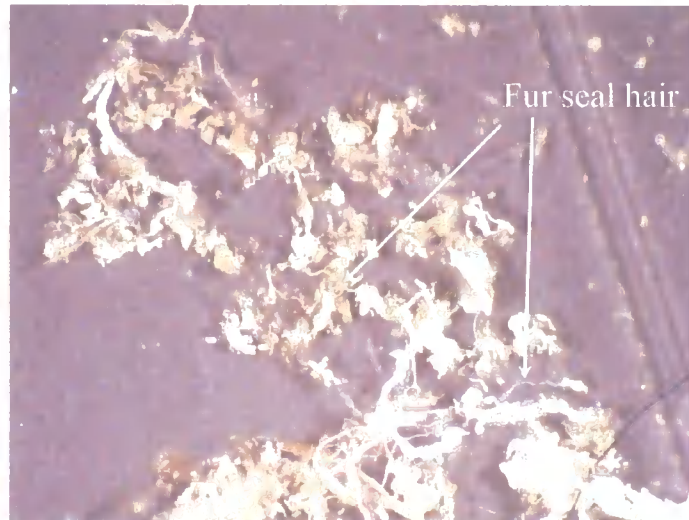


Figure 3.4: Fur seal hair after preparation, as seen under a low- power dissecting microscope (magnification 4 times).



Figure 3.5: An individual fur seal hair separated from organic material, as seen under a low power dissecting microscope (magnification 4 times)

### 3.4 Geochemical analysis

Geochemistry has also been used to aid reconstructions of past fur seal populations (Sun *et al.* 2004a). It is widely established that biological activity alters the chemistry of the soil (Zale 1994a; Lewis- Smith 1988; Zale and Karlen 1989; Hawes 1990; Ellis- Evans 1990) and thereby provides an indication of species survival relative to time (Engstrom and Wright 1984). Based on this theory, Sun *et al.* (2004a) correlate changes in fur seal hair abundance with fluctuations in geochemistry to infer fur seal population fluctuations at King George Island for the past 1500 years. To date this is the only study to have used this as a means to reconstruct fur seal populations, however, geochemistry has been extensively used to reconstruct penguin populations and climate in the Antarctic and Sub- Antarctic islands through the Holocene (Sun *et al.* 2004b; Sun *et al.* 2000; Zale 1994a, b; Zale and Karlen 1989).

#### 3.4.1 Fur seal geochemistry

Sun *et al.* (2004a) used geochemical analysis to infer fur seal population fluctuations (see figure 3.6). They established that the organic matter in sediments at King George Island was marine origin and likely to have originated from seal excrement. Geochemical variations in sediments influenced by seal excrement are closely associated with historical seal population changes, providing an indirect measure of historical fur seal populations. Reconstructions of penguin populations have correlated a range of different elements with fur seal populations at different sites therefore, it cannot be assumed that the elements which Sun *et al.* (2004a) used to reconstruct the fur seal populations at King George Island will be the same at South Georgia. As Zhu *et al.* (2005) indicate, the results from one study may be different to other similar studies due to the site-specific nature of ecological and environmental factors.

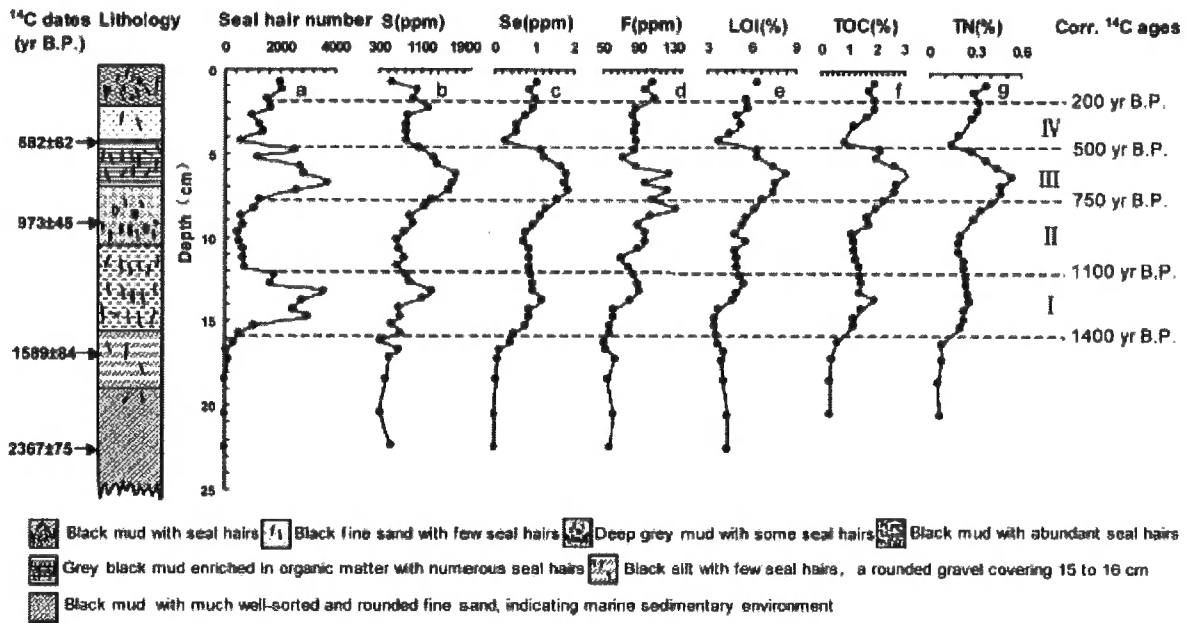


Figure 3.6: Geochemical analyses used to reconstruct fur seal populations (Sun *et al.* 2004a)

As Sun *et al.* (2004a) suggest, the primary factor influencing the geochemistry of the sediment is the chemical composition of the seal excrement. This is enriched in Carbon (C), Oxygen (O), Nitrogen (N) and contains traces of Calcium (Ca), Phosphorus (P), Sulphur (S), Zinc (Zn) and Manganese (Mn) (Pomeroy, P., pers. comm.). The prime factor controlling the chemical composition of the seal excrement is the chemical signature of the prey, which is influenced by the Southern Ocean. As Schlesinger (1991) indicates, the composition of the ocean (see table 3.2) is reflected in the composition of phytoplankton. As krill feed off phytoplankton, the mineral content of krill is similar to that of the ocean. These elements are transferred along the food chain to krill and consequently to fur seals hence, it is likely that fluctuations in these elements will reflect the fur seal population changes.

| Constituent | Concentration in seawater (mg/kg) |
|-------------|-----------------------------------|
| Sodium      | 10,760                            |
| Magnesium   | 1,294                             |
| Calcium     | 412                               |
| Potassium   | 399                               |
| Strontium   | 7.9                               |
| Chloride    | 19,350                            |
| Sulfate     | 2,712                             |
| Bicarbonate | 145                               |
| Bromide     | 67                                |
| Boron       | 4.6                               |
| Fluoride    | 1.3                               |

Table 3.2: Major ion composition of seawater, adapted from Schlesinger (1991).

### 3.4.2 Penguin geochemistry

The use of geochemistry to reconstruct Holocene penguin populations and the associated environmental changes has been extensive (Sun *et al.* 2004b; Sun *et al.* 2000; Zale 1994a, 1994b; Zale and Karlen 1989). As the food source for fur seals and penguins is krill (*Euphausia superba*) (Reid and Croxall 2001; Barlow *et al.* 2002), it can be inferred that similar bio-elements will correlate with fur seal populations as penguin populations.

Zale (1994) found in an analysis of 18 elements from sediment at Hope Bay that concentrations of Calcium (Ca), Cadmium (Cd), Copper (Cu), Phosphorus (P), Strontium (Sr) and Zinc (Zn) were elevated in areas with a higher penguin density. As Sun *et al.* (2004b) indicate, this change is due to the increase in deposition of penguin droppings that strongly influences the physical and chemical properties of soils via the effects of microbes. Elements found to reflect changing penguin populations from a range of studies are shown in table 3.3. As these elements are common in many penguin reconstructions, these elements are susceptible to changes in biology and therefore, it is possible that fluctuations in these elements may reflect changes in fur seal populations.

|  |  |   |   |
|--|--|---|---|
| Sun <i>et al.</i> (2004a)<br>(Fur Seals) | Zale (1994): Hope Bay<br>(Adélie Penguins) | Zhu <i>et al.</i> (2005): Barton Peninsula<br>(Gentoo Penguins) | Sun <i>et al.</i> (2004b): Ardley Island<br>(Penguin) |
| Sulphur (S)                              | Calcium (Ca)                               | Calcium (Ca)  | Calcium (Ca)  |
| Selenium (Se)                            | Phosphorus (P)                             | Phosphorus (P)  | Phosphorus (P)  |
| Fluorine (F)                             | Copper (Cu)                                | Copper (Cu)   | Copper (Cu)   |
| Total Nitrogen (TN)                      | Zinc (Zn)                                  | Zinc (Zn)   | Zinc (Zn)   |
| Total Organic Carbon (TOC)               | Strontium (Sr)                             | Strontium (Sr)  | Strontium (Sr)  |
|  | Cadmium (Cd)                               | Sulphur (S)   | Sulphur (S)   |
|  |  | Selenium (Se)   | Selenium (Se)   |
|  |  | Fluorine (F)  | Fluorine (F)  |
|  |  | Barium (Ba)   |   |

Table 3.3: Element concentration increases that correlate with increases in penguin populations compared to element concentrations found to increase with fur seal populations in Sun *et al.* (2004a).

### 3.4.3 Geochemical hypotheses

Due to time restrictions and the amount of sediment available, it was not possible to test for all elements that may increase with fur seal population growth. To reduce the number to evaluate, I used results from previous studies to hypothesize which elements may be indicative of fur seal populations (see table 3.4).

Following Sun *et al.* (2004a), I tested for the following elements, Carbon, Nitrogen, Sulphur and Selenium. Fluorine was not tested for due to restrictions on the instrument and the limited sample size available. Analysis of the same elements as Sun *et al.* (2004a) helps to determine whether these elements are indicative of fur seal populations throughout the sub Antarctic and not restricted to King George Island. In addition to these elements, I tested for elements that commonly correlate with penguin populations (see table 3.4); Calcium, Copper, Zinc, Strontium and Cadmium. Although Phosphorous concentrations are a common penguin bio indicator, due to the amount of sample available this could not be tested for. Based on the widely recognised hypothesis that abundant ions in seawater will be passed along the food chain to fur seals, I also tested for sodium.

| Element                            | Method of analysis                                     | Reason for analysis                              |
|------------------------------------|--|--|
| Carbon (TOC, Total organic carbon) | Total carbon analyser, elemental combustion system.    | Sun <i>et al.</i> (2004)                         |
| Nitrogen (TN, total nitrogen)      | Elemental combustion system (Costech instruments)      | Sun <i>et al.</i> (2004)                         |
| Sulphur (S)                        | Elemental combustion system (Costech instruments)      | Sun <i>et al.</i> (2004)                         |
| Selenium (Se)                      | ICP- MS (Inductively Coupled Plasma Mass Spectrometer) | Sun <i>et al.</i> (2004)                         |
| Calcium (Ca)                       | ICP- MS  | Zale (1994); Sun <i>et al.</i> (2004b); Seawater |
| Copper (Cu)                        | ICP- MS  | Zale (1994); Sun <i>et al.</i> (2004b)           |
| Zinc (Zn)                          | ICP- MS  | Zale (1994); Sun <i>et al.</i> (2004b)           |
| Cadmium (Cd)                       | ICP- MS  | Zale (1994)                                      |
| Strontium (Sr)                     | ICP- MS  | Zale (1994); Sun <i>et al.</i> (2004b); seawater |
| Manganese (Mn)                     | ICP- MS  | Pomeroy, P., (pers.com.)                         |
| Sodium (Na)                        | ICP- MS  | Seawater   |

Table 3.4: Elements identified as possible bio indicators of fur seal presence.

Although it is possible that these elements may fluctuate with fur seal presence, there are a number of additional factors that may cause concentrations to fluctuate and hence, obscure the fur seal signature thus, the behaviour and environmental pathways of the elements must first be considered.

#### 3.4.3.1 Carbon

Carbon (CO<sub>2</sub>) is fundamental in photosynthesis and respiration hence, indicative of organic productivity within a catchment (total organic carbon (TOC)). Carbonate rocks are also a source of Carbon therefore, concentrations may increase as weathering of

carbonate catchments increases (total inorganic carbon (TIC)). Without determining the difference between TOC and TIC, it is difficult to determine the source of Carbon in the catchment. As Sun *et al.* (2004) highlight, TOC correlates significantly with fur seal hair abundance and is hence, a bio indicator of fur seal presence.

#### 3.4.3.2 Nitrogen

As Nitrogen is an essential constituent of all organisms and represents a key nutrient, it is expected that the concentration of Nitrogen in fur seals would be significant enough to influence the geochemistry of the catchment (Talbot 2001). In studies of moss communities in the Antarctic, the primary source of Nitrogen has been found to be penguin and seal activity, suggesting that biology influences Nitrogen concentrations. Studies of penguin populations have indicated that Nitrogen concentrations are closely correlated with penguin populations and Nitrogen has been used as a proxy for penguin populations (Zhu *et al.* 2005; Christie 1987).

#### 3.4.3.3 Sulphur

Sun *et al.*'s (2004) study of King George Island suggests a close correlation between Sulphur and fur seal hair abundance. As Holmer and Storkholm (2001) indicate, deposition of Sulphur increases in eutrophic lakes. As eutrophication is a consequence of an increasing fur seal population, it is likely that the concentration of Sulphur associated with the eutrophication will indirectly reflect fur seal populations (Lewis-Smith 1988).

#### 3.4.3.4 Selenium

As Ugolini (1972) indicates, the bioavailability of Selenium in animals is determined by other factors such as pH, redox conditions, soil texture, mineralogy and organic matter content. As there are so many influential factors affecting the concentration of Selenium, it is difficult to distinguish the fur seal component. However, as Selenium is one of the elements Sun *et al.* (2004) found to correlate with fur seal hair abundance, it may be a useful bio indicator of fur seal presence at South Georgia.

#### 3.4.3.5 Zinc

As Andrews *et al.* (1996) establish, Zinc has a clear biological function and evidence from previous studies suggests Zinc is highly enriched and significantly correlated to

other biogeochemical markers (Sulphur, Calcium, Copper, Selenium, Strontium, Barium and Fluorine). As a result, Zinc has been used as a proxy for fluctuations in penguin populations (see Sun *et al.* 2004b; Zhu *et al.* 2005 and Zale 1994).

#### 3.4.3.6 Copper

In previous biogeochemical studies, Copper has been used as an indicator for penguin activity and is commonly correlated with Zinc and to a lesser extent Selenium (Zhu *et al.* 2005). Schlesinger (1991) highlight this link between Copper biological activity is due to high concentration in phytoplankton. Copper is incorporated into sediments as the organisms die and sink to deeper waters. Yet as Matsumoto (1993) indicates, a major source of copper within sediments is also chemical weathering. This double usage poses problems for interpretation however, the association of Copper with Zinc in past analyses of bio indicators suggests that Copper concentrations are dominantly influenced by bioactivity (Zale 1994; Zhu *et al.* 2005).

#### 3.4.3.7 Strontium

Reimann and de Caritat (1998) indicate that the environmental paths for Strontium are sea spray, weathering and the dissolution of calcium carbonate, suggesting very little organic influence (Abollino *et al.* 2004). This implies that Strontium is more indicative of environmental change rather than a change in organic matter. Nonetheless, Zale (1994) and Zhu *et al.* (2005) suggest that Strontium is a bio indicator for penguins. As penguins have a similar diet to fur seals, it would be expected that similar elements would be present in fur seal excrement as penguin guano. Sun *et al.* (2004b) also came to this conclusion as the concentration of Strontium in the lake sediments within close proximity to penguin populations is elevated compared to other lake sediments in the maritime Antarctic.

#### 3.4.3.8 Cadmium

Research suggests that Cadmium is closely associated with Zinc however, it does not have a biological role (Reimann and de Caritat 1998). Cadmium displays nutrient like behaviour as it is inadvertently taken up during biological processes (Andrews *et al.* 1996). Due to these properties, it is likely that Cadmium is a good indicator of biological processes. Although in previous studies, Cadmium is not commonly

recognised commonly as a bio indicator, Zale (1994) establishes a correlation between Cadmium and penguin activity.

#### 3.4.3.9 Sodium

As Schlesinger (1991) highlights, Sodium is very abundant in seawater, with concentrations reaching 10, 760 parts per million (ppm) (see table 3.2). As fur seals spend the majority of their life in the ocean, the movement of the seals onto land is likely to increase the amount of seawater on land and hence, increase Sodium concentrations. However, as Reimann and de Caritat (1998) indicate, there are a number of potential pathways for Sodium. Firstly sodium concentrations are likely to increase in the catchment if sea level rises and the catchment becomes submerged. Secondly, if sea spray increases reflecting a climatic change in wind direction and/ or strength this will increase the concentration of Sodium in the catchment. Thirdly, Sodium is abundant in allogenic clastics eroded from catchments therefore; it is a useful element to assess weathering, soil development and erosion in a catchment (Last and Smol 2001). As Engstrom and Wright (1984) suggest, values are higher in late glacial sediments compared to those in postglacial sediments, therefore, providing a useful indicator of deglaciation. As there are a number of potential sources of Sodium and concentrations vary with a variety of processes, concentrations must be analysed in association with other elements, to reduce the potential error in interpretation.

#### 3.4.3.10 Calcium

A number of geochemical studies used to reconstruct past penguin populations have found Calcium to be highly correlated with penguin populations (Zale 1994). However, Ugolini (1972) suggest that Calcium concentrations are relatively low in guano layers and therefore, perhaps not indicative of penguin or other bioactivity. Further studies suggest that Calcium is a common element that occurs in most lake sediments and ground water hence, intimately linked to the carbon and nitrogen cycles (Ito 2001). As Engstrom and Wright (1984) highlight, the primary source of Calcium in lake sediments are allogenic clastics eroded from catchment soils and rocks. The ratio of  $\text{Na}:(\text{Na}+\text{Cl})$  can be used to discriminate between rain and weathering sources and hence, an indicator of weathering processes in the catchment (Andrews *et al.* 1996). As Calcium could potentially be related to fur seal activity, it is necessary to distinguish the influence of

Calcium from other sources in the catchment before evaluating the impact fur seals have upon the concentration.

#### 3.4.3.11 Manganese

Studies suggest that Manganese concentrations are elevated in fur seal excrement and therefore, it can be inferred that concentrations would increase with fur seal presence (Pomeroy, P. pers. com.). Chemical weathering is also a major source of Manganese, hence, to distinguish whether Manganese concentrations are indicative of fur seal presence or weathering, concentrations must correlate with fur seal hair abundance and other bio elements, thus, Manganese cannot be used solely as a proxy for fur seal populations (Reimann and de Caritat 1998; Matsumoto 1993).

#### 3.4.4 ICP-MS hypotheses

Although the elements outlined in table 3.4 are the primary elements I tested for, the ICP-MS used to test for the majority of the metals outlined above, it also provides concentrations for a total of 29 metals from the same sample (see table 3.5). As a consequence of this, all these elements have been analysed to firstly assess the applicability as an indicator of fur seal presence and secondly to provide an indication of any environmental changes at the study site.

| Analyte           | Symbol | Mass |
|-------------------|--------|------|
| Lithium           | Li     | 7    |
| Beryllium         | Be     | 9    |
| Boron             | B      | 11   |
| <b>Sodium*</b>    | Na     | 23   |
| Aluminium         | Al     | 27   |
| Potassium         | K      | 39   |
| <b>Calcium*</b>   | Ca     | 44   |
| Titanium          | Ti     | 48   |
| Vanadium          | V      | 51   |
| Chromium          | Cr     | 52   |
| Iron              | Fe     | 54   |
| <b>Manganese*</b> | Mn     | 55   |
| Iron              | Fe     | 57   |
| Nickel            | Ni     | 58   |
| Cobalt            | Co     | 59   |
| <b>Copper*</b>    | Cu     | 63   |
| <b>Zinc*</b>      | Zn     | 64   |
| Arsenic           | As     | 75   |
| <b>Selenium*</b>  | Se     | 82   |
| <b>Strontium*</b> | Sr     | 88   |
| Molybdenum        | Mo     | 98   |
| Silver            | Ag     | 107  |
| <b>Cadmium*</b>   | Cd     | 114  |
| Antimony          | Sb     | 121  |
| Barium            | Ba     | 138  |
| Thallium          | Tl     | 205  |
| Lead              | Pb     | 206  |
| Lead              | Pb     | 207  |
| Lead              | Pb     | 208  |
| Bismuth           | Bi     | 209  |

Table 3.5: Elements concentrations available from the ICP-MS (\* (and bold) indicates the elements hypothesized as indicators of fur seal presence).

Although these elements may not reflect fur seal presence, they provide an indication of the catchment conditions through the core relative to the fur seal population, hence, allowing the correlation between fur seal populations and changing environmental conditions to be determined.

#### 3.4.4.1 Aluminium

Aluminium is generally associated with an increase in groundwater influx (Abollino *et al.* 2004). If the pH in the catchment is low or high, Aluminium is more soluble and

hence, concentrations increase (Itkonen *et al.* 1999; Andrews *et al.* 1996). This alteration of pH may be associated with an increase in fur seal activity and hence, fur seal presence may indirectly affect the concentrations.

#### 3.4.4.2 Potassium

An enrichment of Potassium can be a result of a number of factors including atmospheric salts, glacial and snow melt waters, rock weathering and groundwater. As these elements are all non-organic elements, it is unlikely that fluctuations in Potassium will reflect fur seal presence in the catchment (Matsumoto 1993; Abollino *et al.* 2004).

#### 3.4.4.3 Titanium

Very little is known about Titanium in lake sediments, and there are no studies to suggest that Titanium would increase with fur seal abundance. Titanium is very abundant in the earth's crust and geogenic dust is the main source of Titanium in the environment, suggesting that it is not indicative of fur seal presence (Marshall and Fairbridge 1999).

#### 3.4.4.4 Barium

In terms of the overall geochemical cycle Barium most closely follows Strontium and Calcium (Marshall and Fairbridge 1999). Using this theory, as Strontium has correlated previously with fur seal abundance, it can be inferred that Ba has the potential to. There is however, debate to the conditions causing an increase in Barium. As Marshall and Fairbridge (1999) indicate, Barium rich areas commonly underlie zones of intense biological activity and occur near ocean ridges. Studies of Antarctic lakes however, suggest an increase with calcite and fluorite, implying a strong correlation with Aluminium, Chromium, Calcium and Silicon, elements not previously found to be bio indicators.

#### 3.4.4.5 Iron, Lithium, Vanadium and Chromium

These elements are considered essential for biology, therefore, it is possible that these elements may correlate with fur seal abundance, yet neither has previously been linked to biological activity (Reimann and de Caritat 1998). Vanadium is a minor element in lake sediments and very little work has been done on the mechanisms causing it to

fluctuate however, the main environmental pathways for Vanadium are weathering and geogenic dust hence, it is unlikely that concentrations will reflect fur seal presence (Reimann and Caritat 1998). The main environmental pathway for Iron is rock weathering, therefore, Iron is likely to be more indicative of the weathering in the catchment rather than fur seal presence (Reimann and de Caritat 1998) Although Chromium is an essential nutrient at low concentrations and it can potentially accumulate in aquatic life (Reimann and de Caritat 1998), previous studies of penguin bio elements have not found Chromium to fluctuate with the changes in biology (Zale 1994; Zhu *et al.* 2005).

#### 3.4.4.6 Molybdenum

There is debate as to how Molybdenum concentrations fluctuate in lake sediments. Firstly Molybdenum is considered essential for biology but it is also a conservative element that has little interaction with biological cycles and hence, is unlikely to fluctuate significantly with fur seal population changes (Andrews *et al.* 1996). Secondly, as Abollino *et al.* (2004) indicate, Molybdenum concentrations increase with sea spray and the presence of rocks hence, reflecting an increase in weathering or change in climate. As Molybdenum fluctuates variety of processes, it cannot be used solely to determine fur seal population fluctuations.

#### 3.4.4.7 Thallium

Although Thallium is considered non-essential for biology, it does have a strong tendency to accumulate in aquatic life therefore, it is possible that Thallium accumulates in krill and hence fur seals (Reimann and de Caritat 1998). However, Reimann and de Caritat (1998) also highlight that Thallium is easily released during weathering hence, this double source makes interpretation difficult.

#### 3.4.4.8 Other elements

The other elements are rare elements and previous geochemical studies using geochemistry as a proxy for past penguin and seal populations do not consider these elements, thus, there is very little literature on how these elements may fluctuate in lake sediments.



## 3.4.5 Geochemical summary

Table 3.6 summarises the elements to be tested, the primary hypotheses for these elements and the method of analysis.

| Element          | Method of analysis                                 | Hypothesis   | Previous Studies   |
|------------------|--|--|--|
| Carbon (TOC; TC) | Elemental combustion system, Total carbon analyser | Fundamental in respiration   | Sun <i>et al.</i> (2004a)  |
| Nitrogen         | Elemental combustion system                        | Essential to organisms   | Sun <i>et al.</i> (2004a)  |
| Sulphur          | Elemental combustion system                        | Increase in eutrophic lakes  | Sun <i>et al.</i> (2004a,b); Zhu <i>et al.</i> (2005)              |
| Selenium         | ICP- MS  | Previous studies suggest a correlation with fur seal abundance.        | Sun <i>et al.</i> (2004a,b); Zhu <i>et al.</i> (2005)              |
| Calcium          | ICP- MS  | Seawater   | Zale (1994); Sun <i>et al.</i> (2004b); Zhu <i>et al.</i> (2005)   |
| Copper           | ICP- MS  | Required by phytoplankton<br>Chemical weathering                       | Zale (1994); Sun <i>et al.</i> (2004a,b); Zhu <i>et al.</i> (2005) |
| Zinc             | ICP- MS  | Strong biological function   | Zale (1994); Sun <i>et al.</i> (2004b); Zhu <i>et al.</i> (2005)   |
| Cadmium          | ICP- MS  | Nutrient like behaviour  | Zale (1994)  |
| Strontium        | ICP- MS  | Sea spray  | Zale (1994); Sun <i>et al.</i> (2004b); Zhu <i>et al.</i> (2005)   |
| Manganese        | ICP- MS  | Pomeroy, P. (pers.com.)  |  |
| Sodium           | ICP- MS  | Seawater   |  |
| Lithium          | ICP- MS  | Essential for biology  |  |
| Beryllium        | ICP- MS  | Unknown  |  |
| Boron            | ICP- MS  | Unknown  |  |
| Aluminium        | ICP- MS  | Increased with groundwater   |  |
| Potassium        | ICP- MS  | Enriched in groundwater  |  |
| Titanium         | ICP- MS  | Abundant in earths crust   |  |
| Vanadium         | ICP- MS  | Essential for biology  |  |
| Chromium         | ICP- MS  | Essential for biology  |  |
| Iron             | ICP- MS  | Essential for biology<br>Weathering-is a primary environmental pathway |  |
| Nickel           | ICP- MS  | Unknown  |  |
| Cobalt           | ICP- MS  | Unknown  |  |
| Arsenic          | ICP- MS  | Unknown  |  |

|            |         |                            |                          |
|------------|---------|----------------------------|--------------------------|
| Molybdenum | ICP- MS | Essential for biology      |                          |
| Silver     | ICP- MS | Unknown                    |                          |
| Antimony   | ICP- MS | Unknown                    |                          |
| Barium     | ICP- MS | Follows Sr                 | Zhu <i>et al.</i> (2005) |
| Thallium   | ICP- MS | Accumulate in aquatic life |                          |
| Lead       | ICP- MS | Unknown                    |                          |
| Bismuth    | ICP- MS | Unknown                    |                          |

Table 3.6: A summary of the elements tested for, the method used in analysis, possible causes fluctuations and the use of the element in previous studies of bio indicators in the sub Antarctic region.

### 3.4.6 Methodology

To prepare the samples for analysis, all samples were freeze-dried. Samples were frozen at  $-80^{\circ}\text{C}$  for 48 hours before being placed in a freeze drier with a vacuum of 1.030 mbar for 16 hours. The samples were then ground in a ball mill at 600 rpm for 5 minutes and stored in a dessicator before use. Table 3.6 summarises elements tested and the method of analysis.

#### 3.4.6.1 Elemental Combustion System

The Elemental Combustion System uses a chromatography method to test for Carbon, Nitrogen and Sulphur. Approximately 10mg of sample was weighed out to two decimal places. The sample was placed in a foil capsule and sealed before being combusted in the Elemental Combustion System (Costech) for 15 minutes. All samples in one run were prepared on the day the machine was run and placed in the carousel before starting any analysis to ensure atmospheric gases would not contaminate the results. When the element is combusted, different elements are released as gases at different times; therefore, the concentration of these elements can be calculated (see Lewis 1997 for further details). To ensure the calibration of the machine was correct, standards were run at the start, end and after every 20 samples in each run.

#### 3.4.6.2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

Element concentrations in samples were measured using an Elan DRC, Inductively Coupled Plasma Mass Spectrometer (IPC-MS). This technique allows a large number of elements in a small sample size to be detected with relatively low detection limits (Jarvis 1997). Samples were firstly freeze-dried and ball milled using the procedure

outlined above. The samples were then digested using the EPA 3051 method before being placed in the ICP-MS.

#### 3.4.6.2.1 EPA 3051 Method

Approximately 250mg of dry sample was weighed out for digestion into a fluorocarbon sample vessel. The amount of sample used varied depending upon the amount of sample available after the other tests had been carried out therefore, in some cases only 50mg of sample was used. To each sample 2ml of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was added and left until the reaction was finished. As the samples were particularly organic, an additional 2ml of  $\text{H}_2\text{O}_2$  was added. Once the reaction stopped, 2ml of hydrochloric acid (HCL) and 9ml of nitric acid ( $\text{HNO}_3$ ) were added. The cap of the sample vessel was put on straight away as there were no carbonates in the samples.

Once the reaction stopped, samples were put in a microwave (CEM MARSSX) for 10 minutes. The sample was then filtered through qualitative filter paper using dilute nitric acid (10% v/v). After filtering, the sample was diluted 1000 times before being run through the ICP-MS (see Jarvis 1997 for further information). For detection of certain elements, ammonia was used as a reaction gas. After every 20 samples, a standard was put through the machine to ensure the calibration was correct.

#### 3.4.6.3 Total Organic Carbon (TOC)

From the results of the elemental combustion system, the amount of total carbon (TC) in each sample was known. To calculate the total organic carbon (TOC) content in the sample, the amount of total inorganic carbon (TIC) was calculated and subtracted from the total carbon (TC) concentrations, calculated using the Elemental Combustion System as outlined above. Although TOC could be calculated independently the TIC method was not as time consuming and gave the same result.

Due to the limited sample sizes, there was not enough sample to test every sample for TIC therefore, 6 samples were selected from the core based upon the TC results (e.g. a sample from a section of high TC, low TC and average TC, ensuring they were all evenly spaced through the core). These samples were then freeze-dried and ball milled as outlined in section 3.4.4. Between 10 and 15mg of each sample was weighed out into a small glass capsule before being placed in the Total Carbon Analyser (TOC 1200).

Each sample was left to react for a minimum of 240 seconds or until the reaction stopped. Initial tests of 2 samples (MAIV/K 50-51 and HUM3 179-179.5) suggested that the concentration was very low and therefore, all the samples were run on the low bench section of the machine, as detection limits were 1ppm. Before any samples were run a standard of  $\text{NaCO}_3$ :  $\text{NaHCO}_3$  (2.2061:1.748) with concentrations of 100ppm, 50ppm and 10ppm was run to provide a calibration for the samples.

#### 3.4.6.4 Summary

Using the multiproxy approach of fur seal hair abundance and geochemistry improves the robustness of the results, reduces error and reduces the influence of local factors on each proxy, hence, prevents the assumption that correlation is equal to causation. For example, as Engstrom and Wright (1984) outline, geochemical analyses can provide evidence for climate change therefore, the geochemical record produced from my results may be reflecting climate change or change in penguin populations rather than a change in fur seal population. However, correlating the geochemical changes with the fur seal hair abundance will provide more robust evidence for fur seal populations. This will help to determine which chemicals reflect a change in fur seal populations and the chemicals which can be used as a proxy in further research without using the time consuming method of calculating the hair abundance.

### 3.5 Dating

To fulfil objective 3 (To determine whether the recent (20<sup>th</sup> –21<sup>st</sup> century) increases in fur seals have exceeded the range of natural variability of past populations), the section of the core that represents this time period must be found and therefore, it is necessary that the core is dated. Further dating was also necessary to fulfil objective 5 (To determine the factors controlling fur seal population changes at South Georgia through the late Holocene), so the fur seal and geochemical data can be correlated with the climate data outlined in section 2.3 and hence, allowing the factors controlling fur seal population changes to be determined.

### 3.5.1 Principles of radiocarbon dating

Radiocarbon dating is a widely used technique for accurately calculating ages up to 45,000 years BP; therefore, this technique is applicable for dating the majority of the core. Radiocarbon dating is only accurate to at least 50 years and often error is greater therefore, due to the dynamic changes in the 20<sup>th</sup> Century, it was necessary to use an alternative technique for the upper part of the core hence, <sup>210</sup>Pb and <sup>137</sup>Cs dating methods were used on the top section of the core.

#### 3.5.1.1 Radiocarbon dating methodology

Three samples in the core were dated. Firstly the base of HUM3 (189-189.5 cm) was dated to determine the time span of the whole core. This sample was sent to NERC radiocarbon laboratories for AMS dating. The sample was firstly digested in 2M HCL at 80°C for 8 hours before being washed free from mineral acid with deionised water. The sample was then dried under a vacuum (200 mbar) at 40°C for 16 hours before being homogenised.

From the results of the fur seal hair abundance and geochemical data, two additional samples at points of significant change were selected for radiocarbon dating and sent to BETA Analytic for AMS dating. These samples were sieved through an 180µm sieve. The bulk sediment sample fraction greater than 180 µm, composed of woody/plant remains was treated as the woody/plant remains were not considered intrusive. Following sieving, the sample was dispersed in deionised water, then washed in hot HCl acid to eliminate carbonates and NaOH to remove secondary organic acids. This was followed by an additional alkali wash to neutralise the solution prior to drying.

### 3.5.2 <sup>210</sup>Pb and <sup>137</sup>Cs dating

The sealing industry began at South Georgia in the late 18<sup>th</sup> century and it was from this time that rapid changes in the fur seal population took place. Determining the exact timing of this change within the core will allow the magnitude of this fluctuation to be compared to previous population changes and therefore, determine whether an event such as this as happened previously. Radiocarbon dates in the 20<sup>th</sup> century can be problematic due to the reworking of sediments, precision issues and the carbon 'bomb'

effect during this time hence, it is widely recognised that radiocarbon dates during the 20<sup>th</sup> century are not accurate enough to provide robust dates. To provide a more accurate indication of the dates at the top of the core, <sup>210</sup>Pb and <sup>137</sup>Cs dating techniques were used.

### 3.5.2.1 Principles of <sup>210</sup>Pb dating

<sup>210</sup>Pb dating has been widely used to date very recent sediment sequences spanning the past 100 to 200 years and is increasingly the backbone upon which recent sedimentation time-scales depend upon (Walker 2005; Appleby and Oldfield 1982). The principle of the dating method is based on the escape of radon gas from the earth into the atmosphere and into sediments (Walker 2005). As the radon gas is an unstable isotope <sup>222</sup>Rn, with a half-life of 3.8 days, it rapidly decays. This rapid decay produces a number of daughter isotopes that decay with very short half-lives until the isotope <sup>210</sup>Pb is reached (see figure 3.7) (Olsson 1986). Measuring the ratio of <sup>210</sup>Pb:<sup>206</sup>Pb in sediments allows the time period since the lead was deposited to be determined and hence, the rate of accumulation can be established (Walker 2005).

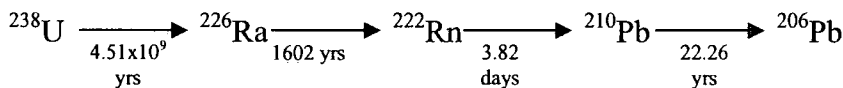


Figure 3.7: <sup>238</sup>U decay series to form the daughter isotope <sup>210</sup>Pb. Time beneath the arrows indicates the half-life of each element.

Problems arise with the method as <sup>210</sup>Pb accumulates in the sediments through two different mechanisms. Firstly, <sup>210</sup>Pb enters the catchment from the in wash of <sup>226</sup>Rn into the lake or sediments. This is consequently incorporated into the sediment and decays to form <sup>210</sup>Pb. This is termed supported <sup>210</sup>Pb. Secondly, <sup>210</sup>Pb, accumulates as a result of <sup>226</sup>Rn decaying prior to sediment incorporation and hence, <sup>210</sup>Pb itself is washed into the catchment. This is termed unsupported <sup>210</sup>Pb (Appleby and Oldfield 1982). In dating, it is the unsupported <sup>210</sup>Pb that is used to calculate the age of the sediments as once incorporated into the sediment it decays exponentially with time (Oldfield and Appleby 1978). The supported <sup>210</sup>Pb is calculated by the assay of the <sup>226</sup>Ra in the sediment, and therefore, this provides an estimate of the amount of <sup>226</sup>Ra washed into the lake/sediment that has not yet decayed into <sup>210</sup>Pb. Subtracting the supported <sup>210</sup>Pb from the

total  $^{210}\text{Pb}$  provides the unsupported  $^{210}\text{Pb}$  used in dating the sediment (Oldfield and Appleby 1978).

### 3.5.2.2 Principles of $^{137}\text{Cs}$ dating

The concentration of  $^{137}\text{Cs}$  in lake sediments is widely used as a distinctive time-stratigraphic marker horizon in sediment sequences (Walker 2005).  $^{137}\text{Cs}$  concentrations increased from the fall out of testing atomic weapons after the Second World War. This caused a peak of  $^{137}\text{Cs}$  in the records in 1963 (Batterbee 1991; Olsson 1986). This known peak in the record can be used to supplement  $^{210}\text{Pb}$  dating, providing a check for the  $^{210}\text{Pb}$  timescale (Walker 2005).

### 3.5.2.3 Methodology for $^{210}\text{Pb}$ and $^{137}\text{Cs}$ dating

All samples were frozen at  $-80^{\circ}\text{C}$  for 48 hours before being placed in a freeze drier with a vacuum of 1.030 for 16 hours. The samples were then ground in a ball mill at 600 rpm for 5 minutes and stored in a dessicator before use. Approximately 0.35 mg of sediment was weighed into small plastic tubes before being placed in an Ortec Gamma Well Detector (GWL series, High purity germanium, coaxial well photon detector system) for two days. After two days, the sample was removed and the  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  counts were recorded.

## 3.6 Sources and magnitude of error

Although the methodology outlined above attempts to minimise the error in the data, it is not possible to fully eliminate error hence, this must highlighted and considered in analysis.

### 3.6.1 Seal hair abundance

Hairs were treated to improve the ease of counting however, it is possible that some hairs may have been lost in this process through transferring sediment between different vessels. As all samples were treated in the same way, this error should be systematic through the core and hence, not affect relative abundance.

To express the hairs per 1 g of dry weight (following Hodgson *et al.* 1998 method), approximately 0.1g of sediment was weighed and treated before counting. However, multiplying the counts by a factor of 10 also increases the error by a factor of 10. To determine the effect this error would have upon the samples, different weights of sample (0.1, 0.2 and 0.3 g) were prepared for 2 samples through the core and counted to evaluate the error in the scaling up process. Results suggested that the initial weight did not alter the overall count therefore, due to the limited amount of sediment available, 0.1g of sediment was used and scaled up.

To ensure that the number of hairs counted was accurate, some samples were counted twice to determine the counting error. All the samples tested showed significant reduction in the amount of hairs when counted as second time. To ensure this error was not specific to some samples, all samples were counted a second time. The difference between the two samples at all intervals throughout the core was both large and systematic and so cast doubt on the results. To reduce any uncertainty, *all* the samples were recounted a third time. The third counts were very similar to the second counts (see appendix 1). As the first counts were a magnitude higher than the following counts, I omitted the first counts in the results, and took an average of the second and third counts. The anomalous first counts are thought to be a result of adapting the technique and an incorrect identification of hairs and mistaking organic material for hairs. The standard deviations of the second and third counts for each sample were calculated and an average of all the standard deviations was used to calculate the average error of the whole data set (see appendix 1).

### 3.6.2 Geochemistry

#### 3.6.2.1 Elemental combustion system (Nitrogen, Carbon and Sulphur)

Each sample was tested twice and the average of the two values was taken. This ensured that in the machine or the effect of contamination would be eliminated. For any sample where the two values in the same run had a difference greater than 1%, the sample was run again, until this error was reduced (see appendix 2). As samples were weighed to 2 decimal places, the results are expressed to 2 decimal places.

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### 3.6.2.2 ICP-MS

After every 20 samples, a standard was run to ensure the calibration was still correct. The calibration of Ag was not reliable and therefore, the results of the Ag concentrations will not be considered. As Ag has not been found previously as a bio indicator, it was not time-efficient to run the samples again to obtain concentrations for Ag.

### 3.7 Summary

This chapter has outlined the development of the methodology used to calculate fur seal hair abundance and a methodology to determine the concentrations of elements that are possible indicators of fur seal presence. The following chapter will outline the results obtained from this methodology.

# Chapter 4

## Results

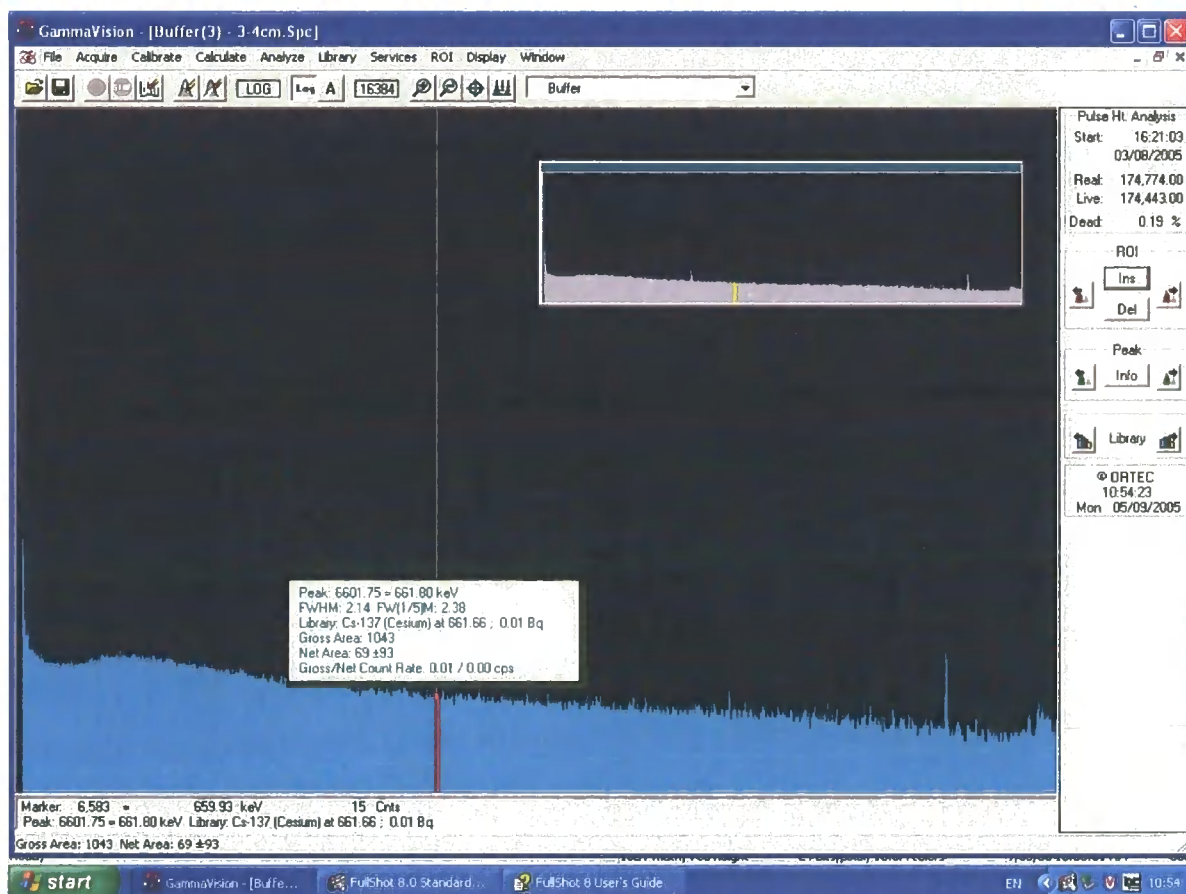


Plate 4: Results of the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  analysis.

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## 4: Results

This chapter outlines my results on which my analysis in chapter 5 is based upon. Firstly I will consider factors to account for when analysing the results. This will be followed by a stratigraphic and sedimentological description of the core followed by the results of the fur seal hair abundance and the geochemical analysis before the results from the radiocarbon dating and  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  dating are addressed. Finally I consider how the dating results can be applied to form an age model.

### 4.1 Core Stratigraphy

As there are two separate cores used in the study, these were analysed individually prior to any analysis to provide a broad indication of the sedimentological changes prior to analysis.

#### 4.1.1 HUM3

At the base of the core, the sediment is light grey, unsaturated material. This clay is present for 2cm, before a clean transition to darker sediment. Using Troels- Smith (1955) analysis, this 2cm thick basal unit can be classified as Argilla Steatodes (As). Above the clay, the sediment is very dark, inelastic and horizontal bedding planes are visible. In this sediment, there are fragments of primarily herbaceous material, although there are also some small fragments of wood. The sediment is almost homogenous throughout the core, gradually becoming darker and increasingly saturated. Throughout the core organic fragments upto 2cm in length are visible. Very small clastics are also noticeable giving some sub samples a grittier texture. All the sediment in this section of the core can be described as Detritus Lignosis (DI) (ibid). As noted in chapter 2, there is the potential that the lake was previously marine due to isostatic changes following the LGM. However, sedimentological analysis indicates there is no evidence of marine sediments in the core hence, implying that the lake has been freshwater for at least the past 3500  $^{14}\text{C}$  yrs BP.

#### 4.1.2 MAIVIK

The sediment in the core when extracted was very saturated and homogenous, hence, a detailed Troels – Smith analysis was not undertaken. There were no clear stratifications or changes in the sediment composition. The entire core was classified as Detritus Lignosis (DL), nigror degree 4, stratification 0, siccitas 1 and elasticitas 2.

#### 4.1.3 Implications for analysis

As no palaeocological analysis was done on the primary transition at the base of the core the cause of this change in sedimentation is unknown. However, this sedimentological change will be considered in analysis and related to the age model to allow this transition to be analysed with proxy environmental changes and therefore, allowing potential causes of this change to be inferred.

#### 4.2 Depth Scale

In this section, depths are expressed relative to the whole core as I have outlined in section 3.1.1 (equation 3.1).

#### 4.3 Fur seal hair abundance

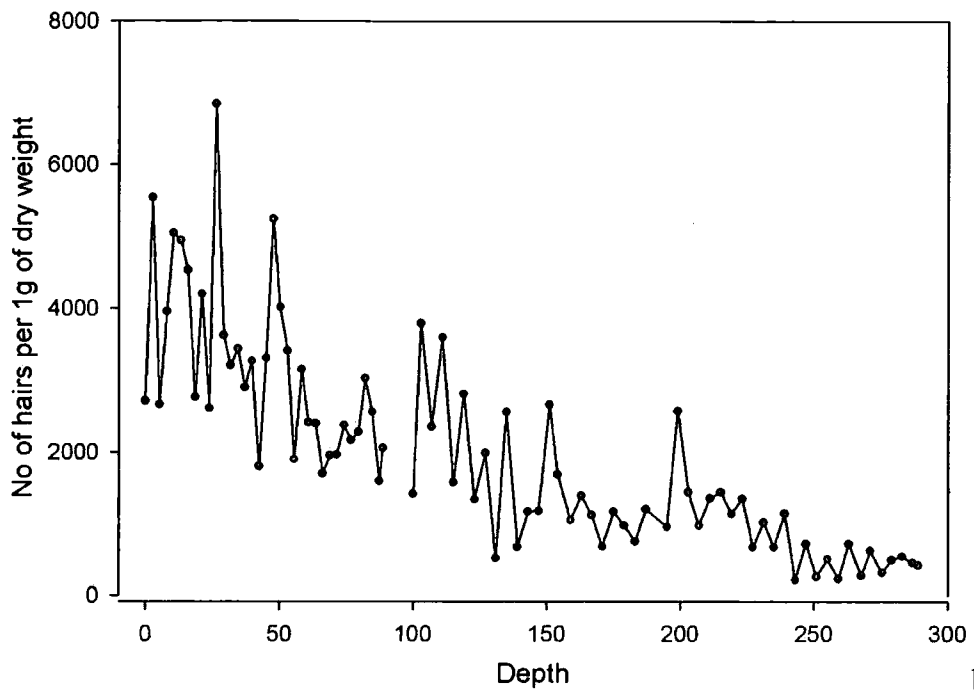
Figure 4.1 shows the fur seal hair counts relative to depth. At the base of the core the hairs are in low abundance, fluctuating between 250 hairs to 700 hairs per 1 g of dry weight, but remaining relatively constant in comparison to the remainder of the core. The hairs remain at this level to a depth of 243 cm, when hair abundance begins to increase gradually from 221 hairs to 2464 hairs at 191 cm. Following this increase, the hairs remain at a relatively constant level to 139 cm. A small decrease is observed from 187 cm to 163 cm, reaching a minimum at 171 cm as hairs decrease to 687 hairs per 1 g of dry weight. Following this brief decline, hairs increase to 2666 at 151 cm, before declining again to levels similar to those before the peak. From 131 cm the number of hairs per 1 g of dry weight increases to 3795 at 103 cm.

After the gap in the core record a 3-point increase to 3330 hairs at 79.4 cm is observed. Following this increase, hair abundance declines to 1705 hairs at 66.2 cm, with a small interruption at 71.5 cm, as hairs increase again to 2913 hairs. From this minimum, hairs

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increase to a peak at 47.6 cm of 5244 hairs. This increase is constant with the exception of a small decline at 55.6 cm to 1904. From this maximum, hairs rapidly decline to a minimum of 1805 hairs at 42.4 cm before increasing and remaining relatively constant at 3200 hairs from 39.7 to 29.1 cm. This is followed by a one point increase to the maximum number of hairs for the whole core at 26.5 cm as hairs increase to 6845 before dramatically declining to 2615 hairs at 23.8 cm. Hairs then increase to a smaller peak (5045) at 8 cm. Hairs then decline to 2665 at 5.3 cm before increasing again to almost maximum levels at 2.6 cm as hairs reach 5541. At the top of the core, the number of hairs declines to 2718 hairs at 0 cm.

a)



b)

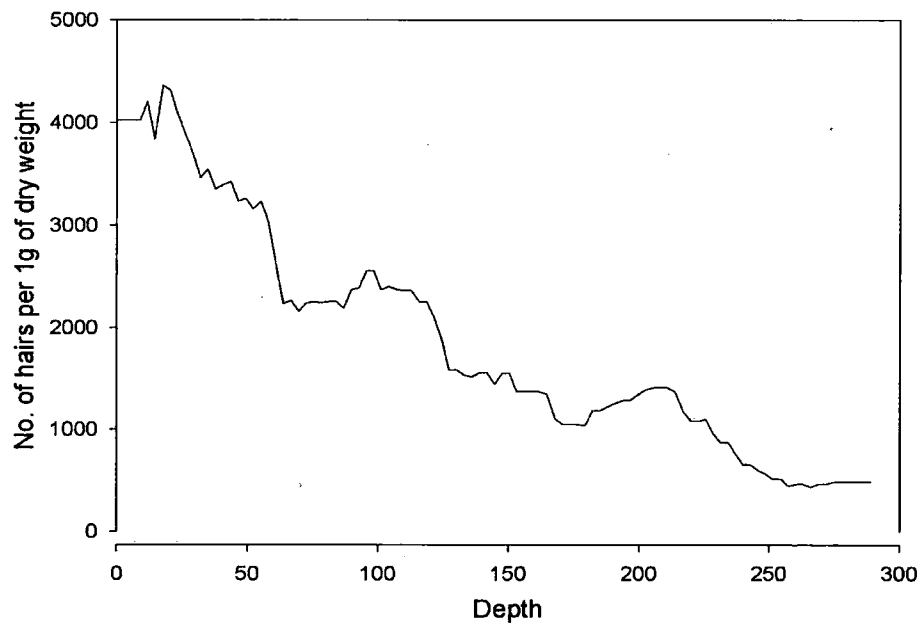


Figure 4.1a): Fur seal hair abundance relative to depth. Note gap (between cores) at depths 90-100 cm. b): Smoothed fur seal hair abundance results. Results were smoothed using Sigma Plot, running average function, with sampling proportions set at 0.1.

The smoothing curve was calculated using running average function in Sigma Plot. In the function running average, the sample proportion was set at 0.1, therefore, an average

is calculated for the data point and the surrounding 10% of the whole data set. As a total of 84 samples were tested, this is equivalent to an 8.4 point running average

#### 4.3.1 Error

The average standard deviation for the whole core is 337.04 hairs (see appendix 1 and figure 4.2). Error for HUM3 core (100-289 cm) is 142.95 hairs, whereas the error for MAIVK (0-68 cm) is slightly higher at 483.92 hairs. Compared to the number of counts the large fluctuations are of a magnitude greater than the error and therefore, can be classed as significant.

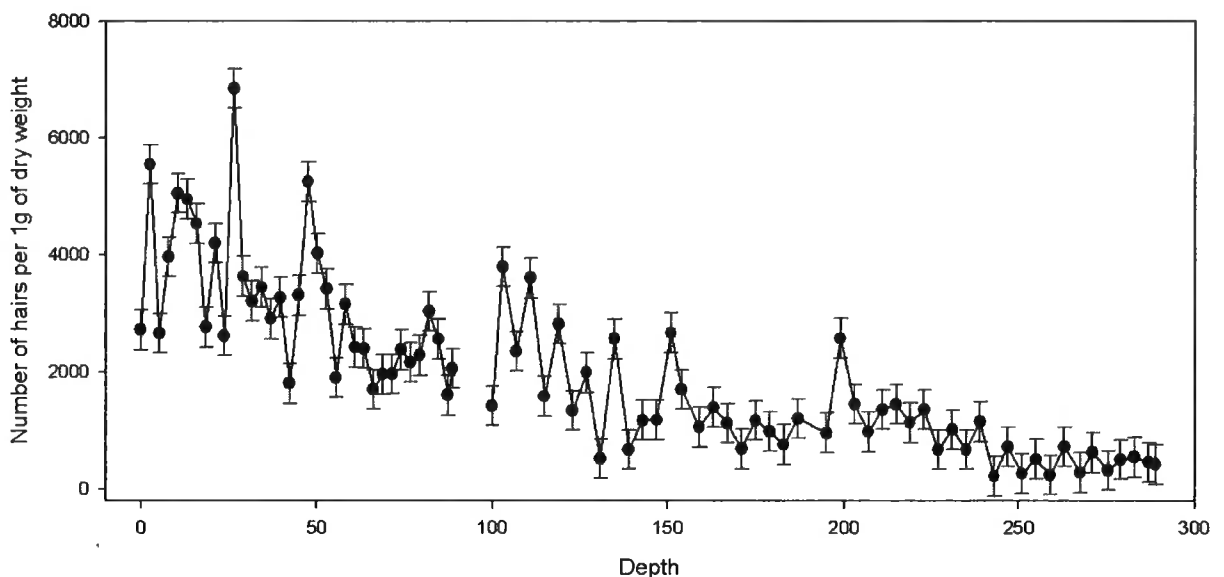


Figure 4.2: Fur seal hair abundance results with error bars. Error is calculated the average standard deviation of all the counts (see section 3.6 and appendix 1).

#### 4.3.2 Summary

Figure 4.1 indicates that hair abundance has increased from the base to the top of the core. This increase has been accelerated with 3 step increases occurring at 250 cm, 125 cm and 66.2 cm (see figure 4.1b). Hairs are relatively low from the base of the core until 250 cm as they begin to increase and plateau at approximately 2000 per 1 g of dry weight. A second significant increase is observed at a depth of 125 cm as hairs increase slightly too approximately 3000 per 1 g of dry weight. The largest change through the

core is then observed at 66.2 cm as the number of hairs rapidly increases to approximately 4000 hairs per 1 g of dry weight at the top of the core.

#### 4.4 Geochemistry

A total of 32 elements have been tested for within the sediments. Carbon (C), Nitrogen (N) and Sulphur (S) concentrations were obtained using an elemental combustion system and concentrations are expressed as percentages. The remaining elements were analysed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and are expressed in parts per billion (ppb).

The elements were grouped together with elements showing similar fluctuations to improve the ease of analysis (see table 4.1).

| Group A        | Group B                      | Group C      | Group D         | Group E                      | Group F      |
|----------------|------------------------------|--------------|-----------------|------------------------------|--------------|
| Nitrogen (N)   | Potassium (K)                | Copper (Cu)  | Bismuth (Bi)    | Selenium (Se)                | Sulphur (S)  |
| Carbon (C)     | Titanium (Ti)                | Zinc (Zn)    | Molybdenum (Mo) | Vanadium (V)                 | Arsenic (As) |
| Strontium (Sr) | Barium (Ba)                  | Cadmium (Cd) | Antimony (Sb)   | Calcium (Ca)                 | Nickel (Ni)  |
| Aluminium      | 57-Iron ( $^{57}\text{Fe}$ ) | Lithium (Li) | Thallium (Tl)   | Chromium (Cr)                |              |
|                | Sodium (Na)                  |              | Boron (B)       | Manganese (Mn)               |              |
|                |                              |              | Beryllium (Be)  | Cobalt (Co)                  |              |
|                |                              |              |                 | 54-Iron ( $^{54}\text{Fe}$ ) |              |

Table 4.1: Element groups, grouped according to their fluctuations through the core.

#### 4.4.1 Group A: Nitrogen (N), Carbon (C), Strontium (Sr), Aluminium (Al) (figure 4.3)

##### 4.4.1.1 Nitrogen

From the base of the core, nitrogen concentrations increase rapidly to a peak of 3.64% at 199 cm. Concentrations remain constant at this level before peaking and reaching maximum concentrations through the whole core of 3.72% at 179 cm. From this peak, the percentage of nitrogen declines slightly, fluctuating around 3% with a significant decline at 175 cm as concentrations fall to 1.91%. Following this relatively stable period, a 5-point decline to 1.61% at 131 cm occurs. After the gap in the record, concentrations remain constant at 3.2% from 88.7 cm to the top of the core, with minor declines to approximately 2.6% at 82.1, 68.8, 59.9 and 0 cm.

#### 4.4.1.2 Carbon

Following Sun *et al.* (2004a), total organic carbon (TOC) is an indicator of fur seal populations. To obtain TOC, total carbon (TC) and total inorganic carbon (TIC) were tested for and used to calculate the TOC (see section 3.4.6.3). The following section presents the results of the TC before the results of the TIC (and hence TOC) results are considered.

##### 4.4.1.2.1 Total Carbon

The percentage of Carbon in the core fluctuates in a similar manner to Nitrogen, increasing from the base of the core to a peak of 41% at 215 cm. From this peak, concentrations decline to 37% and fluctuate at this level from 207 cm to 100 cm. Significant declines occur at 175 cm and 131 cm as concentrations reduce to 19% and 20% respectively. From 90cm, concentrations increase to a peak of 46% at 76.8 cm before plateauing at 41% for the remainder of the core, with the exception of a notable 3-point decline, observed at 52.9 cm, where concentrations decline to 34%.

##### 4.4.1.2.2 Total Organic Carbon (TOC)

To calculate the TOC, the TIC was measured and subtracted from the TC, as outlined in section 3.4.6.3. The TIC results are shown in table 4.2. In the samples tested the percentage of TIC in the sediment was very low (approximately 0.08%), and therefore it can be inferred that the majority of the carbon is organic carbon and only a trace is inorganic carbon.

| Sample          | TIC<br>(mg/kg) | % TIC   |
|-----------------|----------------|---------|
| MAIVK 2-3       | 81.38          | 0.08138 |
| MAIVK 50-51     | 84.9           | 0.0849  |
| HUM 3 179-179.5 | 62.42          | 0.06042 |

Table 4.2: Results of the TIC analysis. Results are given in mg/kg; these were converted into percentages to correlate with the TC results.

The samples were only tested once and for the results to be accurate, the samples should have been repeated. However, as the percentage of TIC is so insignificant, the accuracy

of this is not necessary as the amount of TIC in the sample can be termed a trace and hence, it can be assumed that the TC concentrations represent TOC concentrations.

#### 4.4.1.3 Strontium

From the base of the core, concentrations remain below detection limits (detection limit is 5ppb) until a rapid 3-point increase occurs at 183 cm. This increase peaks at 175 cm as concentrations reach 45,000 ppb, a maximum concentration through the core. Following the peak, rapid declines are observed at 147 and 139 cm as concentrations decline to 0 ppb. Concentrations almost reach maximum levels again at 131 cm (44,000 ppb), before a 4-point decline to 28,500 ppb at 115 cm. This is followed by a small peak at 111 cm (38,200 ppb) before another significant 3-point decline to a minimum at 100 cm. Following the gap in the record, concentrations remain relatively constant at 28,000 ppb from 90 cm to 71.5 cm. A rapid peak is observed at 68.8 cm (44,000 ppb), before a dramatic decline at 58.2 cm to 0 ppb.

#### 4.4.1.4 Aluminium

Concentrations of aluminium remain below detection limits through the base of the core to 183 cm, when a rapid 3-point increase begins, peaking at 20.3 ppm (parts per million) at 179 cm. This peak is followed by a small decline to 11.7 ppm at 169 cm, before concentrations increase again and peak at slightly lower concentrations than previously at 159 cm. This double peak is followed by a dramatic decline at 147 cm and 139 cm as concentrations fall to 0.22 ppm (218,000 ppb) and 0.10 ppm (104,000 ppb) respectively. Concentrations rapidly increase to almost maximum concentrations at 131 cm reaching 22.7 ppm. This peak is followed by a gradual decline to 100 cm interrupted by a small peak at 107 cm as concentrations reach 18 ppm. Following the gap in the data, a 6-point decline is observed to a minimum at 76.8 cm before a 3-point increase to a peak at 52 cm as concentrations reach a maximum of 22.9 ppm. Following this peak, concentrations are below detection at 44 cm before increasing and plateauing at 13 ppm to the top of the core. At the very top of the core, concentrations increase to 19.9 ppm at 0 cm.

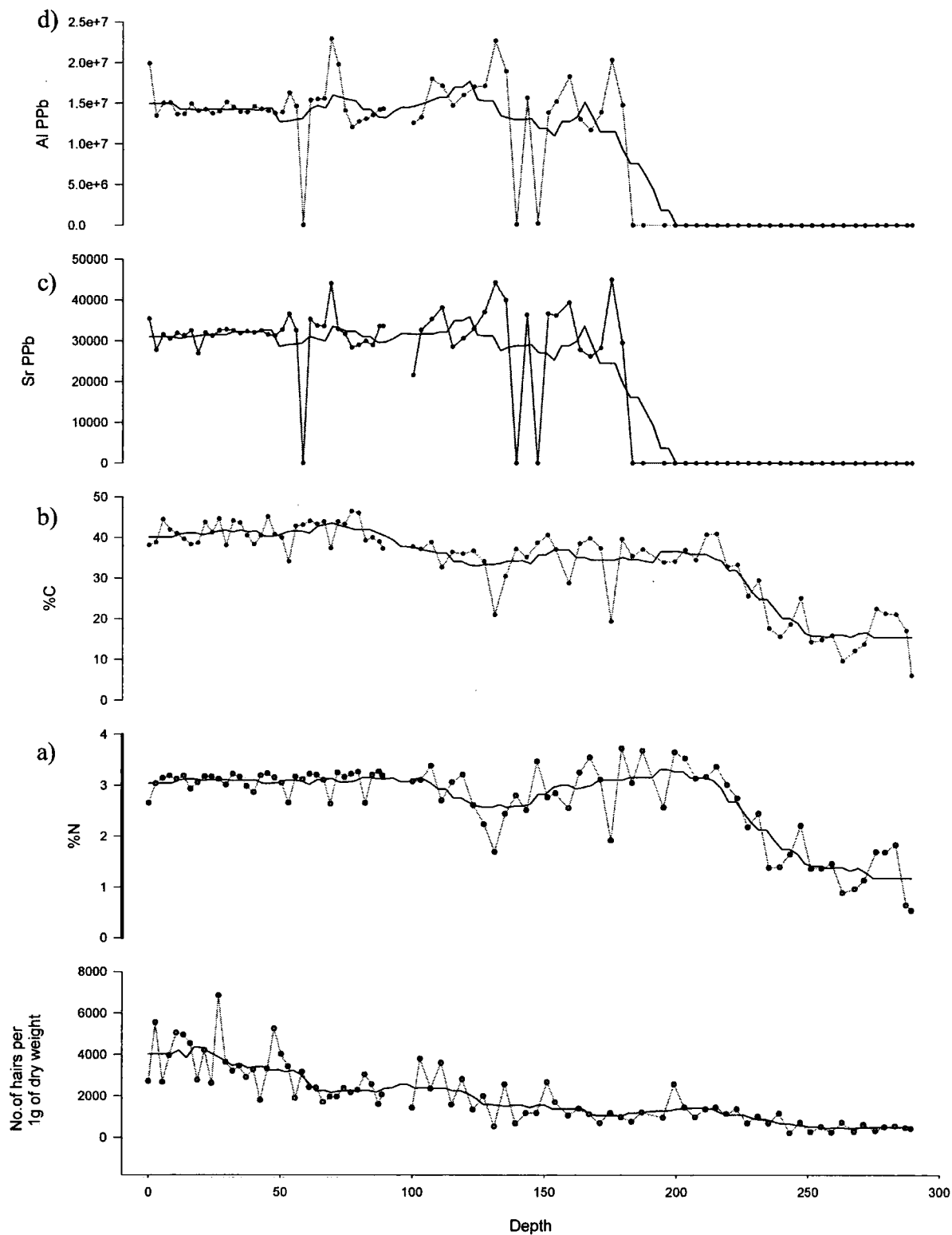


Figure 4.3: Element concentrations of group A compared to fur seal hair abundance. a) Nitrogen; b) Carbon; c) Strontium d) Aluminium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 4.4.1.5 Summary of group A

This group of elements show a dramatic increase at the base of the core, although the increase is delayed in the Aluminium and Strontium record, it is of a similar magnitude to the increase in Carbon and Nitrogen. This rapid increase is the largest change through the core in all of these elements. Following the increase, although Strontium and Aluminium fluctuate slightly, this fluctuation is no greater than 10 ppm.

#### 4.4.2 Group B: Potassium (K), Titanium (Ti), Barium (Ba), Iron 57 ( $^{57}\text{Fe}$ ) and Sodium (Na) (figure 4.4)

##### 4.4.2.1 Potassium

From the base of the core concentrations remain below detection limits until 207 cm, as a rapid 7-point increase begins. Concentrations increase from 0.03ppm (33,600 ppb) at 207 cm to 6.4 ppm at 175 cm. Following this peak, concentrations fluctuate significantly with troughs at 167 cm, 155 cm and 139 cm as concentrations fall to approximately 2 ppb. Maximum concentrations occur at 131 cm (6.9 ppm) before concentrations fall and remain constant at 4 ppm to 100 cm. After the gap in the record, a 6-point decline is observed to a minimum at 60 cm. Concentrations peak at 68.8 cm at 4 ppm ppb before dramatically declining to 0 ppm at 58.2 cm. Concentrations then rise again and remain constant at 1.9 ppm to the top of the core.

##### 4.4.2.2 Titanium

Concentrations remain at below detection limits from the base of the core to 183 cm, when concentrations rapidly increase to a peak of 3 ppm at 175 cm. Although the increase is not as rapid as seen in the concentration of Potassium, the magnitude is similar and peaks at the same point within the core. Following this peak, concentrations decline and fluctuate around 1.3 ppm, with the exception of a smaller peak at 159 cm to 2.4 ppm. A dramatic decline occurs at 147 cm and 139 cm as concentrations fall below detection limits. Concentrations then increase to a maximum of 3.8 ppm at 131 cm. From this maximum concentrations decline gradually (with the exception of a small peak at 107cm) to 1.5 ppm at 100 cm. At the base of MAIVK core, concentrations decline continuously from 2 ppm at 90 cm to 1 ppm at 71.5 cm with the exception of a

small peak at 74.1 cm. From this point, concentrations plateau at 1.1 ppm to the top of the core, with the exception of a dramatic decline to below detection limits at 58.2 cm.

#### 4.4.2.3 Barium

The concentration of Barium is very similar to the fluctuations in Titanium, as concentrations remain below detection limits from the base of the core to 183 cm. At 183 cm concentrations begin to increase and peak at 82,000 ppb at 175 cm. Following this peak, concentrations fall and fluctuate around 40,000 ppb. A peak at 159 cm interrupts this briefly as concentrations increase to 65,600 ppb. A dramatic decline in concentration is observed at 147 and 139 cm as seen in the Titanium record, before a rapid increase at 131 cm to maximum concentrations through the whole core of 91,800 ppb. Following this peak, concentrations decline to a minimum at 115 cm of 47,700 ppb before a small peak of 66,000 ppb at 107 cm. After the gap in the record, concentrations decline from 90 cm to 79.4 cm before increasing to 56,000 ppb at 68.8 cm. From this point concentrations decline to below detection limits ppb at 58.2 cm before increasing and plateauing at 35,000 ppb to the top of the core. At the very top of the core, concentrations increase to 56,000 ppb.

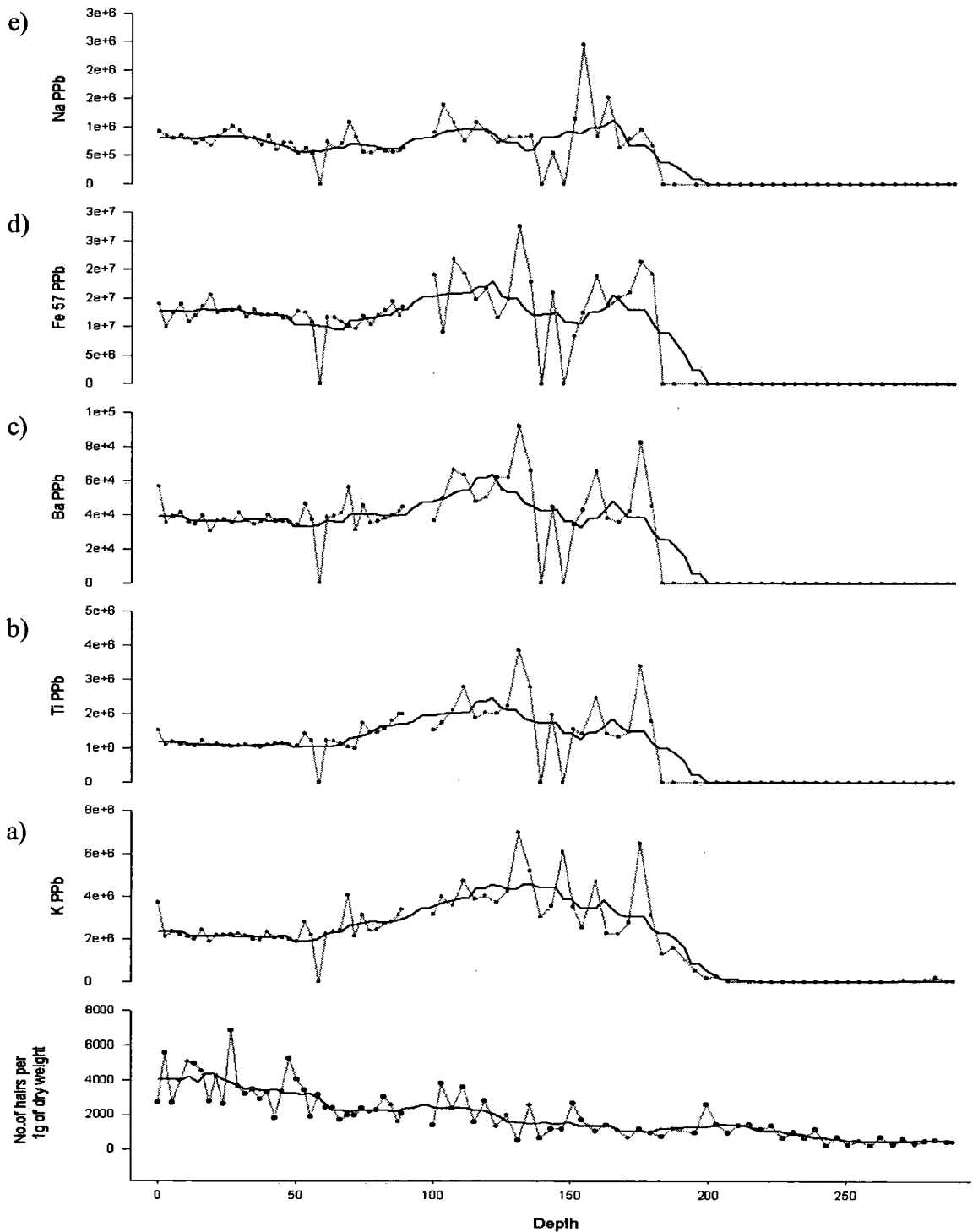


Figure 4.4: Element concentrations of group B compared to fur seal hair abundance. a) Potassium; b) Thallium; c) Barium; d) 57- Iron; e) Sodium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 4.4.2.4 <sup>57</sup>Fe-Iron

<sup>57</sup>Fe fluctuates in a similar manner to Potassium, Barium and Titanium with concentrations remaining at 0 ppb from the base of the core to 183 cm and increasing rapidly to a peak at 175 cm of 21 ppm. This is followed by a dramatic decline to below detection limits is seen at 147 cm and 139 cm before a rapid increase at 131 cm, as concentrations reach the maximum within the core of 27 ppm. <sup>57</sup>Fe concentrations decline to a minimum at 123 cm before peaking at 107 cm as concentrations reach 21 ppm. Following the gap in the record, concentrations decline to below detection limits at 58.2 cm before plateauing at 12 ppm from 50.3 cm to the top of the core.

#### 4.3.2.1 Sodium

Concentrations again remain below detection limits through the base of the core until 183 cm when concentrations increase to 960,000 ppb at 175 cm. Concentrations decline slightly to a minimum at 167 cm before peaking at 163 cm, which is followed by a larger peak at 154 cm as concentrations reach maximum concentrations of 2 ppm (2,000,000 ppb). After peaking, concentrations rapidly decline to below detection limits at 147 cm and 139 cm, following the same trend as the other elements in the group. Following the decline, concentrations increase to smaller peaks of 1 ppm (1,000,000 ppb) at 115 cm and 103 cm, peaks not observed in the other element concentrations in this series. After the gap in the record, concentrations remain relatively constant from 90 cm to 74.1 cm, peaking at 68.8 cm at 1 ppm. Concentrations then decline rapidly to below detection at 58.2 cm, before gradually increasing to a small peak at 26.5 cm. From this peak, concentrations decline slightly to 18.5 cm before gradually increasing again to 900,000 ppb at the top of the core.

#### 4.4.2.5 Summary of group B

This group of elements show a significant increase from below detection at 183 cm to a peak at 175 cm. Following this rapid increase, concentrations decline slightly to a minimum at 147 and 139 cm. Concentrations then reach a maximum at 131 cm. Following the gap in the record, a peak at 68.8 cm is observed in most element

concentrations before a decline at 58.2 cm. Concentrations then remain relatively constant to the top of the core.

#### 4.4.3 Group C: Copper (Cu), Zinc (Zn), Cadmium (Cd) and Lithium (Li) (See figure 4.5)

##### 4.4.3.1 Copper

Concentrations remain at below detection from the base of the core to 179 cm, when a small increase to 40,000 ppb is observed which is maintained to 155 cm before concentrations decline to 0 ppb. Concentrations remain below detection limits with the exception of two small peaks at 127 cm and 111 cm to 19,000 ppb. The next significant change occurs at 84.7 cm as copper begins to gradually increase from below detection limits. At 74.1 cm following the gradual increase, concentrations rapidly increase from 10,000 ppb to a maximum (309,400 ppb) at 68.8 cm. From this maximum, the concentration of copper declines rapidly to below detection limits at 58.2 cm before peaking at 40 cm at 24,000 ppb. Concentrations then plateau from 50.3 cm to 2.6 cm, fluctuating between 19,000 ppb and 23,000 ppb. In the top 2.6 cm of the core concentrations increase slightly to 281,700 ppb, reaching a similar level to the concentration observed at 52 cm.

##### 4.4.3.2 Zinc

Zinc concentrations remain minimal from the base of the core to 175 cm. From 175 cm concentrations increase from 14,800 ppb to a peak of 544,000 ppb at 183 cm. Following a small decline to a minimum at 167 cm, concentrations peak at a similar level to 183 cm at 159 cm. Concentrations decline to below detection limits at 147 cm and 139 cm. Following this double trough, concentrations increase to a peak at 131 cm before declining and reaching a minimum at 123 cm. From this minimum, concentrations increase again to 424,000 ppb at 107 cm. After the gap in the record, concentrations remain constant until 79.4 cm, when a 4 point increase is observed to a maximum value of 1,500,000 ppb at 71.4 cm. A decline to below detection limits is then witnessed at 58.2 cm as also observed in the copper fluctuations. From this point the concentration of zinc is very similar to the copper concentrations, peaking slightly at 52.9 cm before remaining relatively constant until 2.6 cm, when concentrations increase from 1,100,000 ppb to 1,400,000 ppb at 0 cm.

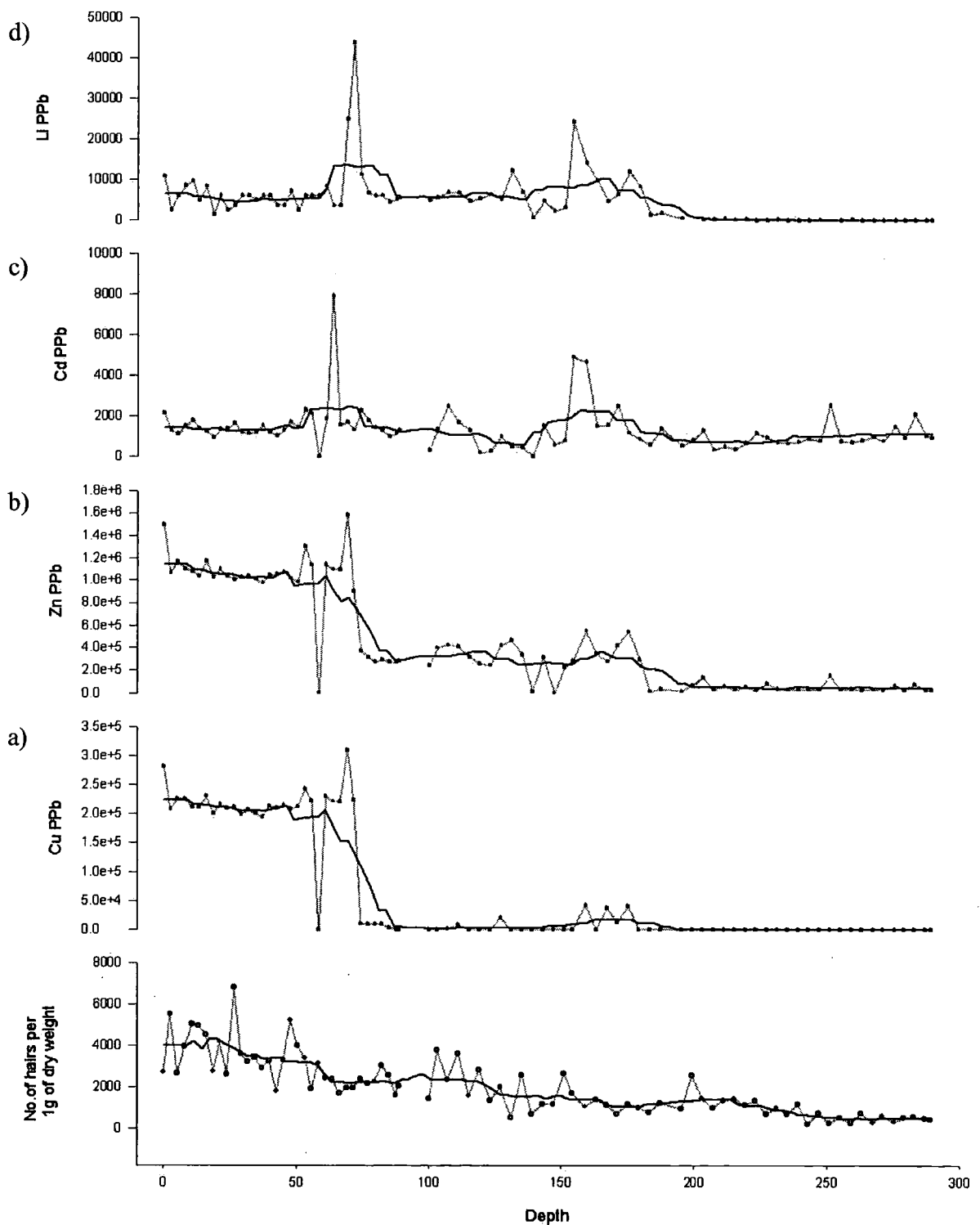


Figure 4.5: Element concentrations of group C compared to fur seal hair abundance. a) Copper; b) Zinc; c) Cadmium; d) Lithium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 4.4.3.3 Cadmium

Cadmium concentrations fluctuate to a greater extent than that observed in the Zinc and Copper concentrations through the base of the core. Concentrations remain at approximately 650 ppb through the base of the core, with the exception of small peaks at 283 cm, 275.5 cm and 251 cm as concentrations reach 2,100 ppb, 1,477 ppb and 2,500 ppb respectively. From 183 cm to 159 cm, concentrations increase from 578 ppb to 4,600 ppb, with concentrations peaking again at 154 cm before declining to approximately 1,000 ppb. A small peak occurs at 143 cm before concentrations decline to 17 ppb at 139 cm. Concentrations remain low until 119 cm when they increase to a peak of 2,500 ppb at 107 cm. Following the gap in the record, concentrations increase from 964 ppb at 84.7 cm to a small peak at 71.4 cm before rapidly increasing from 1,500 ppb to a maximum of 7,900 ppb at 63.5 cm. As observed in the other elements, concentrations then rapidly decline to below detection limits at 58.2 cm. From this decline, concentrations fluctuate around 1,500 ppb for the remainder of the core.

#### 4.4.3.4 Lithium

Lithium concentrations are similar to the rest of this group, as concentrations increase from very low concentrations at the base of the core to 195 cm when concentrations increase to a peak of 12,000 ppb at 175 cm. Although the increase begins slightly earlier than the other element concentrations in this group, the most significant increase commences at 183 cm, similar to the trend observed in the rest of the group. Following a small decline at 167 cm, a 4-point increase to 154 cm is observed as concentrations peak at 24,000 ppb. Concentrations decline to a minimum at 147 cm and 139 cm (as observed in other records) before a small peak at 131 cm as concentrations reach 12,200 ppb. From this point concentrations decline to 500 ppb and remain stable at this level to 100 cm. After the gap in the record, from 90 cm to 82.1 cm concentrations remain at a similar level as to before the gap. From 76.8 cm lithium concentrations increase and reach a maximum at 71.5 cm as concentrations peak at 43,600 ppb. From here concentrations decline and fluctuate around 5,000 ppb to the top of the core. The significant decline observed in the elements in the rest of the group at 58.2 cm is also

observed in the lithium concentrations however, this does not appear as significant as other records as concentrations remain relatively low though the top of the core.

#### 4.4.3.5 Summary of group C

This group of elements show a general trend of a small increase in concentrations commencing at 187 cm, peaking at 175 cm and again at 154 cm. Concentrations decline to a minimum at 139 cm, before increasing and peaking at 131 cm (copper 127 cm) and 107 cm (copper 111 cm). Following the gap in the record, concentrations remain relatively constant until the rapid increase to maximum concentrations at 68.8 cm (Cadmium 63.5 cm and Lithium 71.5 cm). Following the increase, a decline to below detection limits at 58.2 cm is observed in all concentrations. From this rapid decline, concentrations plateau until 2.6 cm, where an increase is observed in all the elements.

#### 4.4.4 Group D: Bismuth (Bi), Molybdenum (Mo), Antimony (Sb), Thallium (Tl), Boron (B), Beryllium (Be) (See figure 4.6)

##### 4.4.4.1 Bismuth

Bismuth concentrations remain at below detection limits through the base of the core to 207 cm, with the exception of small peaks at 263 cm and 251 cm. Concentrations begin to significantly increase at 199 cm, peaking at 154 cm as concentrations reach maximum values through the core of 977 ppb. Concentrations decline rapidly to below detection limits at 147 cm and remain at this level until 2.6 cm as the concentration increases slightly to 66 ppb.

##### 4.4.4.2 Molybdenum

Concentrations of molybdenum remain below detection limits through the base of the core to 183 cm. From 183 cm, concentrations begin to increase to a maximum of 40,000 ppb at 154cm. Following this peak, concentrations rapidly decline to 1,300 ppb at 151 cm and from here remain relatively constant until 84.7 cm. From 84.7 cm, a 6-point increase is observed to 71.5 cm as concentrations peak at 31,800 ppb. Following this peak, concentrations decline to 0 ppb at 58.2 cm and then increase to plateau between 10,000 and 15,000 ppb to the top of the core.

#### 4.4.4.3 Antimony

Concentrations at the base of the core, in contrast to the other elements are relatively high and fluctuating, peaking at 251 cm as concentrations reach 2,800 ppb however, the general trend is decline to a minimum of 0 ppb at 187 cm. From 167 cm the concentration increases and peaks at 2,700 ppb at 159 cm. Following a decline at 155 cm to 401 ppb, concentrations increase again to a maximum at 154 cm of 3,300 ppb. From this peak, concentrations rapidly decline to below detection limits at 151 cm and remain low to 87.4 cm, concentrations increase again from below detection limits at 87.4cm to 1,400 ppb at 74.1 cm. Following this peak, concentrations decline to a minimum of 15 ppb at 44 cm and then plateau at approximately 250 ppb to the top of the core, where a small increase is observed at 0 cm as concentrations increase to 680 ppb.

#### 4.4.4.4 Thallium

At the base of the core thallium concentrations remain below detection limits to 219 cm, with the exception of a small peak at 263 cm and 227 cm. From 219 cm, concentrations increase to a double peak at 203 cm (985 ppb) and 187 cm (1,100 ppb). After this double peak, concentrations decline to 182 ppb at 179 cm. Following this brief fall, concentrations increase again from 167 cm and reach a maximum of 2,700 ppb at 154 cm. From here concentrations decline to 0 ppb at 151 cm and 143 cm, peaking briefly at 147 cm at 1,500 ppb. Concentrations then peak slightly at 139 cm before declining to 60 ppb, remaining relatively constant to 84.7 cm. Concentrations increase to a peak at 71.5 cm as concentrations reach 1,000 ppb. Following the peak concentrations decline to approximately 130 ppb where they remain constant to the top of the core. A slight increase is observed at 58.2 cm to 329 ppb and at 0 cm as concentrations reach 425 ppb.

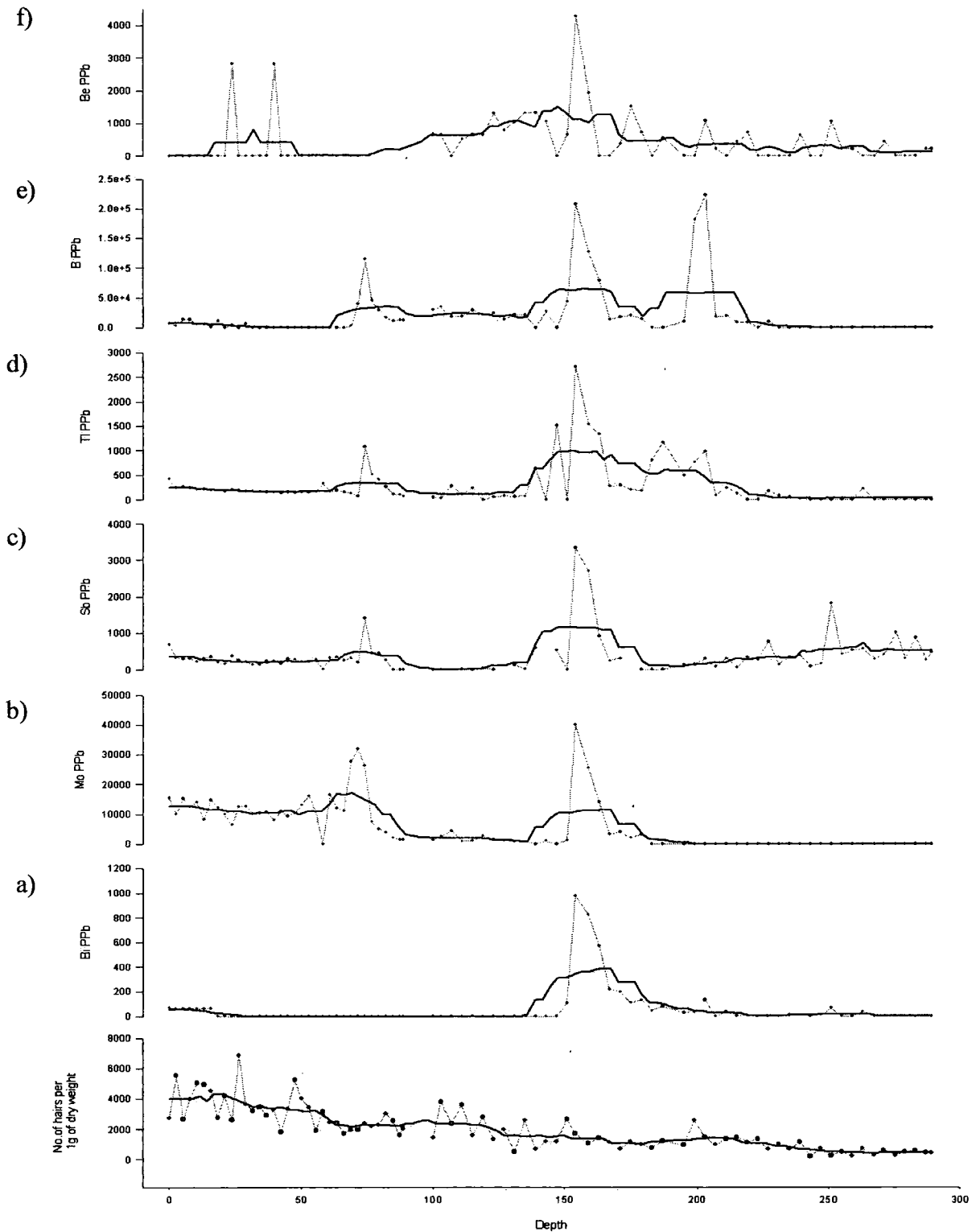


Figure 4.6: Element concentrations of group D compared to fur seal hair abundance. a) Bismuth; b) Molybdenum; c) Antimony; d) Thallium; e) Boron; f) Beryllium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 4.4.4.5 Boron

Concentrations remain below detection limits through the base of the core to 223 cm. From 223 cm, a 5-point increase occurs to a peak at 203 cm as concentrations reach 222,700 ppb, a maximum concentration for the whole core. From this peak, concentrations decline to 9,750 ppb at 195 cm and remain at this level until 167 cm as a second increase begins, peaking at 154 cm (207,000 ppb). Following this second peak, concentrations decline to 0 ppb at 147 cm and 139 cm, before increasing to 20,000 ppb and remaining at this level to 100 cm. From 88.7 cm, a 5-point increase is observed to a peak at 74.1 cm as concentrations reach 114,000 ppb. Following the peak, concentrations decline to below detection limits at 66.2 cm and remain at this level until 21.2 cm. From 21.2 cm, concentrations increase slightly to the top of the core, reaching a maximum 143,000 ppb at 5.3 cm.

#### 4.4.4.6 Beryllium

The record is not continuous however, concentrations fluctuate significantly through the base of the core. The general trend is an increase to a maximum peak of 4,261 ppb at 154 cm. Following the peak, concentrations decline rapidly to approximately 1,000 ppb and remain constant to the gap in the record. Following this gap, concentrations peak at 74.1 cm and 68.8 cm. The only concentrations recorded after this peak are at 39.7 cm and 23.8 cm as concentrations reach 2,800 ppb.

#### 4.4.4.7 Summary of group D

All the elements in this series show relatively low concentrations at the base of the core, with the exception of Antimony, which declines from the base of the core to a minimum at 179 cm. Thallium and Boron show a peak at 203 cm. All the elements show a large increase commencing at 179 cm and peak at maximum concentrations at 154 cm, followed by a rapid decline. With the exception of Bismuth, an additional peak is observed at 74.1 cm, followed by a gradual increase to the top of the core. Beryllium shows the rapid increase at 154 cm however, the decrease from this peak is not as rapid as the other elements and the top of the core does not show the gradual increase as observed in the other elements.

#### 4.4.5 Group E: Selenium (Se), Vanadium (V), Calcium (Ca), Chromium (Cr), Manganese (Mn), Cobalt (Co), Iron 54 (<sup>54</sup>Fe) (See figure 4.7)

##### 4.4.5.1 Selenium

At the base of the core, selenium concentrations are relatively high and decline from 193,100 ppb at 289 cm to 14,300 ppb at 179 cm. A double peak at 283 cm and 275.5 cm interrupts this general decline briefly as concentrations increase to 536,300 ppb and 597,700 ppb respectively. Maximum concentrations are reached at 251 cm as concentrations increase to 848,100 ppb. Following this peak, concentrations decline to previous levels before increasing to 399,000 ppb at 227 cm. This peak is followed by a small decline before an additional peak at 203 cm to 560,000 ppb. From this peak, concentrations decline to 13,000 ppb at 179 cm and remain at low levels until a peak is observed at 147 cm as concentrations increase to 387,000 ppb. A smaller peak at 139 cm follows this before concentrations decline to almost below detection limits at 135 cm. The concentration then remains at this level with the exception of a small interruption at 107 cm. Following the gap in the record, concentrations remain low until 76.8 cm, when a 3-point increase occurs as concentrations peak at 68.8 cm at 325,000 ppb. From this peak there is a rapid decline to a minimum at 58.2 cm of 11,000 ppb. Following this decline, concentrations increase to 214,800 ppb at 53 cm before gradually declining to 103,000 ppb at 2 cm. Concentrations at 0 cm increase slightly from this level to 132,000 ppb.

##### 4.4.5.2 Vanadium

Concentrations of vanadium are very similar to those of selenium, showing a decline in concentration from the base of the core, with a double peak occurring at 283 cm and 275.5 cm, increasing to 1.8 ppm and 1.7 ppm respectively. A significant peak also occurs at 251 cm as concentrations increase to 3 ppm from 629,000 ppb at 255 cm. Following this noteworthy increase, concentrations decline to a 605,000 ppb at 247 cm and continue to gradually decline. Interrupting the gradual decline, as observed in selenium concentrations, are smaller peaks at 117 cm and 203 cm. Following this decline, concentrations remain constant from 179 cm to 151 cm. A peak occurs at 147 cm as concentrations increase to 1 ppm. A smaller peak at 139 cm follows this as concentrations reach 626,000 ppb. Following this point, concentrations remain at below

detection limits from 135 cm to 79.4 cm. At 71.5 cm maximum concentrations are reached as the concentration increases from 0 ppb to 3 ppm. Concentrations then decline rapidly to 0 ppb at 68.8 cm and remain at this level to 26.5 cm, when a gradual increase is observed to the top of the core as concentrations reach 862,000 ppb.

#### 4.4.5.3 Calcium

Calcium shows a similar fluctuation to vanadium and selenium at the base of the core as concentrations decline from 1,300 ppm at 289 cm to 7.2 ppm at 179 cm. The double peak as observed in the concentration of vanadium and selenium is also evident in the Calcium record at 283 cm and 275.5 cm. A peak at 251 cm interrupts the gradual decline from the base of the core as concentrations increase from 1,200 ppm at 255 cm to 6,000 ppm. Following this rapid increase, concentrations return to levels before the increase occurred. A smaller increase is observed at 227 cm, which is followed by slight fluctuations before a larger peak at 203 cm. From this peak, concentrations decline to 7.2 ppm at 179 cm, where concentrations remain to 100 cm, with the exception of two small peaks at 147 cm and 139 cm as concentrations increase to 1,300 ppm and 662 ppm respectively. From 90 cm, to the top of the core concentrations remain constant at approximately 5 ppm.

#### 4.4.5.4 Chromium

Chromium concentrations remain relatively constant at the base of the core at 11,000 ppb. As seen in the rest of the elements within this group, peaks are observed at 283 cm and 275.5 cm and again at 251 cm however, this peak at 251 cm does not reach maximum values for the whole core as shown in the rest of the elements in this group. Following this peak at 251 cm, smaller peaks are observed at 227 cm and 203 cm. A significant peak is also observed at 187 cm, as concentrations increase to 50,733 ppb. From this peak, concentrations decrease to 10,000 ppb and remain constant from 179 cm to 155 cm. At 155 cm concentrations begin a 4-point increase to a maximum of 100,500 ppb at 147 cm. A smaller peak of 46,000 ppb at 139 cm follows this maximum peak. At 135 cm, concentrations decline to 14,000 ppb, which is maintained until 100 cm. From 90 cm, concentrations decline gradually to a minimum of 150 ppb at 58.2 cm, before then increasing to 5,500 ppb, at 55.6 cm and remaining at this level to the top of the core.

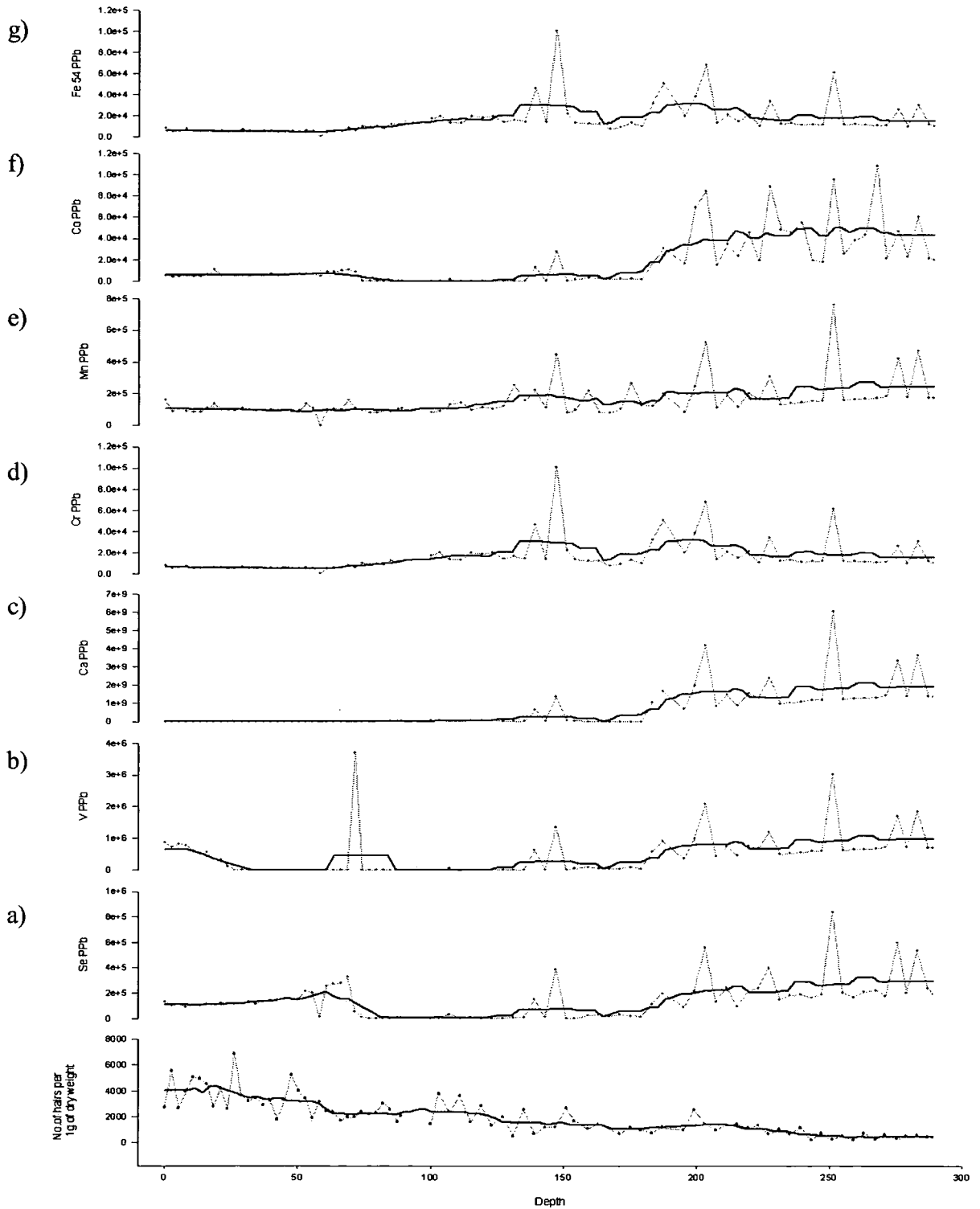


Figure 4.7: Element concentrations of group E compared to fur seal hair abundance. a) Selenium; b) Vanadium; c) Calcium; d) Chromium; e) Manganese; f) Cobalt; g) 54-Iron. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 4.4.5.5 Manganese

Concentrations at the base of the core are at relatively high levels and decline from this point. A double peak at 283 cm and 275.5 cm interrupts this general decline as concentrations increase to approximately 45,000 ppb before maximum concentrations of 759,000 ppb are reached at 251 cm. Following the peak, concentrations decline rapidly to concentrations similar to before the peak. From 231 cm, the concentration of manganese fluctuates significantly. Significant peaks are observed at 227 cm and 203 cm, similar to the other elements in this group. An additional peak is also observed at 147 cm as concentrations increase to 448,000 ppb, yet from here the general trend is decline. From 88.8 cm, concentrations remain at approximately 100,000 ppb. Fluctuations in this section of the core appear insignificant in comparison to the magnitude of changes deeper in the core. However, a small peak occurs at 68.8 cm as concentrations increase to 158,000 ppb and a decline to below detection limits at 58.2 cm. Finally concentrations increase slightly at 0 cm to 160,000 ppb.

#### 4.4.5.6 Cobalt

Concentrations of cobalt at the top of the core are relatively high and although they fluctuate significantly the general trend is one of decline. Peaks observed in the other elements at 283 cm and 275.5 cm occur in the cobalt record however, these peaks are not as significant as others recorded. Maximum concentrations are reached at 267.5 cm as concentrations reach at 108,000 ppb. Following a slight decline, an additional peak occurs at 251 cm (95,700 ppb). Slightly smaller peaks are also observed at 227 cm and 203 cm. Following this peak, concentrations rapidly decline to 1,800 ppb at 179 cm. Concentrations remain at this level to 100 cm, interrupted slightly by a peak at 147 cm and 139 cm. From 90 cm concentrations remain below detection limits to 76.8 cm as concentrations increase slightly to peak at 10,000 ppb at 68.8 cm. Following this small peak, concentrations remain relatively constant to the top of the core with the exception of a small increase at 18.5 cm to 10,700 ppb.

#### 4.4.5.7 54-Iron

Concentrations gradually increase from the base of the core to a maximum of 146.2 ppm at 205 cm. Smaller peaks are also recorded at 283 cm, 275.5 cm and 251 cm as observed in the other elements. From the peak at 205 cm, concentrations decline to 15.8 ppm at 179 cm and remain relatively constant until 100 cm, with a small interruption with peaks at 147 cm and 139 cm. From 88.7 cm to the top of the core concentrations remain constant at approximately 14 ppm, with the exception of 58.2 cm, when concentrations decline to 8,000 ppb (0.008ppm).

#### 4.4.5.8 Summary of group E

This group show a gradual decrease in concentration from the base of the core. This decrease is interrupted in all element concentrations with peaks at 283 cm and 275.5 cm, followed by a larger peak at 251 cm, where maximum concentrations are met or almost met. Following this peak, the correlation between the elements is not as significant however, in all the elements a peak is recorded at 147 cm and 139 cm. Following these peaks, concentrations fall to very low levels and remain constant to 79.4 cm. From this point, all the elements, with the exception of Ca, Cr and <sup>54</sup>Fe peak briefly at 71.5 cm. Following this peak, a rapid decline is observed in all the elements (with the exception of Ca and V) to almost below detection limits at 58.2 cm. Following this rapid decline concentrations increase and remain relatively constant for the remainder of the core.

#### 4.4.6 Group F: Arsenic (As), Sulphur (S), Nickel (Ni) (See figure 4.8)

These elements do not display a similar pattern to any of the element groups therefore, they have been grouped together.

##### 4.4.6.1 Arsenic

Maximum concentrations are reached at 283 cm as concentrations reach 16,700 ppb. Following this peak, concentrations decrease to 726 ppb at 279 cm and then gradually decrease to below detection limits at 227 cm. Concentrations remain at 0ppb until 183 cm, when a rapid increase begins which peaks at 154 cm as concentrations reach 12,600 ppb. Following this increase there is a rapid decline in concentrations to below detection limits at 147 cm. From this low point, concentrations increase to almost maximum

concentrations at 115 cm, which is followed by a smaller peak at 107 cm. After the gap in the record, a 4-point increase is observed to a peak at 82.1 cm at 12,500 ppb. Concentrations then decline to approximately 7,000 ppb, as concentrations plateau to the top of the core, with the exception of a significant decline at 58.2 cm to below detection limits.

#### 4.4.6.2 Sulphur

At the base of the core the sulphur content increases from 0.39% at 289 cm to 2.1% at 279 cm. Following this peak, the concentration of sulphur drops dramatically at 263 cm to 0.48%. The sulphur concentration then gradually increases, peaking at 259 cm and 247 cm before reaching a maximum peak of 3.075% at 227 cm. Following the peak, the content of sulphur gradually declines to a minimum of 0.554% at 175 cm, before increasing again and remaining relatively constant before a decline at 131 cm to 0.78%. From this point, the percentage of sulphur increases again and peaks at 115 cm at similar levels to the peak observed at 227 cm. Following this peak, a smaller peak is observed at 103 cm. After the gap in the record, concentrations reach 2.41% at 90 cm before declining to 0.82% at 82.1 cm. Concentrations gradually increase to a smaller peak of 1.23% at 34.4 cm before a gradual decline to the top of the core.

#### 4.3.6.1 Nickel

Nickel concentrations remain at very low levels from the base of the core to 239 cm, when an increase in concentration begins. The increase is gradual until a peak at 179 cm as concentrations reach 31,700 ppb. The peak is followed by a dramatic decline to below detection limits at 175 cm, followed by a smaller peak at 167 cm (25,300 ppb). Concentrations drop back to below detection limits before increasing and peaking at maximum concentrations of 54,900 ppb at 151 cm. Following maximum concentrations the nickel level fluctuates, peaking at 143, 135 and 127 cm as concentrations reach approximately 17,000 ppb. A 4-point increase, peaking at 107 cm, follows this fluctuation. From 88.6 to 76.8 cm the concentrations fluctuate slightly but remain around the 10,000 ppb before a dramatic decline to 0 ppb at 71.5 cm. Peaks at 66.2 cm and 55.6 cm follow this before declining back to 0 ppb from 53 cm. The concentration of nickel remains at this level until 2.6 cm is reached and concentrations increase to 23,000 ppb.

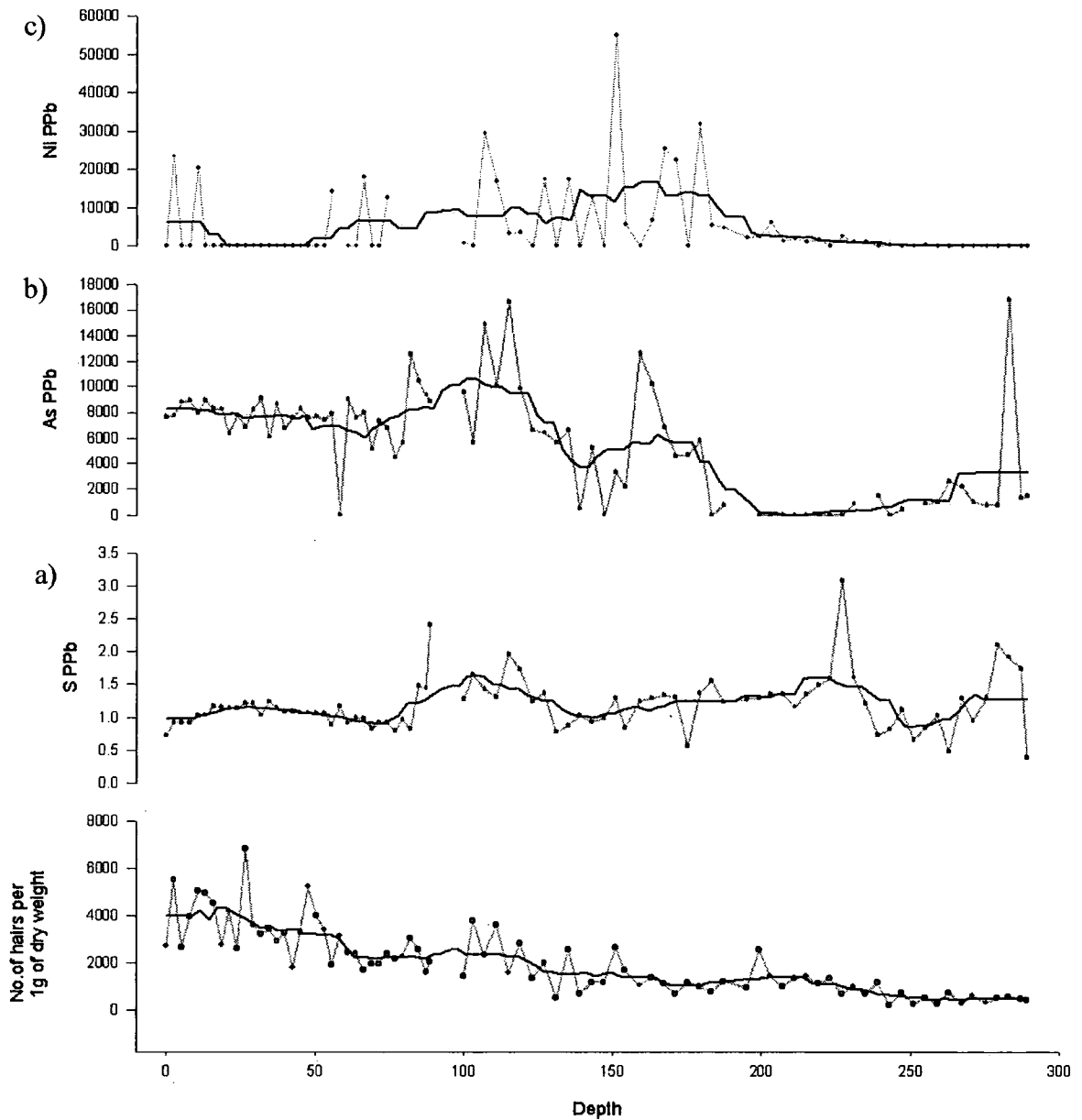


Figure 4.8: Element concentrations of group F compared to fur seal hair abundance. a) Sulphur; b) Arsenic; c) Nickel. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 4.4.7 Summary of geochemical results

The most significant change through the whole core in all the element concentrations occurs near the base of the core. Elements in groups A (Sr, Al), B (K, Ti, Ba,  $^{57}\text{Fe}$ , Na), C (Zn, Cd, Li) and D (Bi, Mo, Sb, Tl, B, Be) all show a dramatic increase in concentrations at 183 cm. Carbon and Nitrogen are the exception to this, as the increase in these elements begins earlier at 263 cm. The elements of group E (Se, V, Ca, Cr, Co  $^{54}\text{Fe}$ ) decline rapidly from the base of the core to very low levels at 179 cm.

The concentrations of elements in groups A and B peak at 175 cm, before declining. In groups C and D, the increase is prolonged and concentrations do not peak until 150 cm. The double trough observed at 147 cm and 139 cm is present in all of the element concentrations in groups A, B, C and D (with the exception of Bi), suggesting a brief but notable change at this point. This change also correlates with the elements negatively correlated with depth (group E), as element concentrations increase to peaks at 147 cm and 139 cm. From this point, the correlation between the element concentrations is not as strong, suggesting smaller changes to the catchment are occurring.

Following the decline at 147 and 139 cm and gradual increase, concentrations decline slightly in most element groups before increasing slightly to a smaller peak. This peak occurs in most element concentrations at 107 cm however, it does range from 111 cm (Ti) to 103 cm (Cr). The elements in group E, negatively correlated with depth, also peak at this point. As all element concentrations increase at this point, it suggests a brief but significant change in the system.

After the gap in the record, a large peak is observed in all the element records. Groups A (Sr, Al), B (K, Ba, Na), C (Cu, Zn), E (Mn, Se) peak at 68.8 cm. Elements in group D peak slightly earlier at 74.1 cm. Although the timing of the peak varies slightly (from 74.1 cm-63.5 cm) all elements display a significant peak at this point, with the most dramatic peaks observed in the Zn and Cu records. Following this peak, all the elements in groups A, B and C display a dramatic decline at 58.2 cm, as concentrations fall to below detection limits. This decline is also observed in some elements in the other groups (Se, Cr, Mn, Mo, Sb, As and  $^{54}\text{Fe}$ ) however, the magnitude is not as significant

as in the other element groups. This dramatic 1-point decline in all the records suggests a significant but very brief change has occurred in the catchment at this point. From this point in the core there are no significant trends common across all elements. However, it can be noted that very few significant changes in comparison to the rest of the core take place in any elements. This implies the catchment has reached stabilisation from 58.2 cm hence, very few changes in element concentration occur.

#### 4.5 Dating

##### 4.5.1 Radiocarbon dating

The base of the core has been radiocarbon dated at 3439 +/- 25 yrs BP (SUERC-2303) using Accelerator Mass Spectrometry (AMS) (Moreton *et al.* unpublished data). From the results of the fur seal hair abundance record and geochemical analysis, samples were chosen to obtain further radiocarbon dates to assist in analysis and help to correlate the change in the fur seal hair abundance and geochemistry to climatic changes occurring within the catchment. Samples HUM3 82-83 cm and MAIVK 50 cm were selected for dating for reasons outlined below.

##### 4.5.1.1 HUM3 82-83 cm

From the results of the hair abundance and geochemical analysis (See figures 4.1, 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8), it is clear that a distinct change occurs at 187 cm (HUM3 87 cm) in the geochemical record and to some extent in the fur seal hair abundance record. Using a constant sedimentation rate model derived the radiocarbon date at the base of the core, this gives a date of approximately 2000<sup>14</sup>C yrs BP which corresponds to a distinct climate change at South Georgia (see figure 2.11). This point in the core appears to be the largest change in the geochemical and fur seal hair abundance record, therefore, it is important to get a radiocarbon date for this point to determine when it occurred and allow correlation with other records which climate changes have been inferred. As this is a distinct change, it is likely that sedimentation rates at this point in the core have altered and therefore, calculating a constant sedimentation rates across this point is likely to incur error. A date from this point will provide a pinning point upon which a constant sedimentation rate can be used for the rest of the core. Although a distinct change occurs at HUM 3 87 cm, after other analysis there was no sample left

at this point therefore, the nearest sample was 82 cm and so this sample was submitted to Beta Analytic for AMS dating.

#### 4.5.1.2 MAIV/K 50-51 cm

The results of the geochemical analysis and the hair abundance record highlight a distinct change at 66.2 cm (MAIV/K 50cm). At this point the fur seal hair abundance begins to increase sharply to a maximum at 47 cm. The geochemical analysis also shows a change at this point as concentrations peak ~ 68 cm before declining to a minimum at 58 cm (see figures 4.3 - 4.8). These rapid changes suggest that a large catchment change is occurring at this point therefore, obtaining a date from this point will help to establish the timing of this change and hence, allowing factors affecting fur seal population fluctuations at this point to be inferred.

The gap between the two cores is problematic, as the amount of shrinkage between the cores is difficult to calculate. As this sample is near the base of the MAIV/K core, this will provide a clearer indication of the timescale missing in the combined cores and reduce the error in calculating constant sedimentation rates. Considering the 2 cores as a whole core, this sample is also nearer the top of the core, and therefore, it is likely that sedimentation rates have changed from the other radiocarbon dated samples. A date at this point in the core is useful to determine sedimentation rates and reduce the error of calculating a constant sedimentation rate from a different core.

These radiocarbon dates will be used to date the rest of the core using a constant sedimentation rate model. However, as figure 3.1 illustrates some of the core has shrunk after extraction. This coupled with the compression of sediments after deposition in the lake means that a sedimentation rate is unlikely to be constant. Although the 3 radiocarbon dates will reduce the error, it must be noted that the fixed spatial resolution used to sample the cores (i.e. 2 cm) will not reflect a fixed temporal resolution used for analysis. For example the core has been sampled every 2 cm; calculating a constant sedimentation rate, 2 cm may appear to represent 10 years however, in some sections of the core a period of increased sedimentation rate may result in 2 cm being deposited in 5 years. During a period of reduced sedimentation rate, 2 cm may be deposited in 20 years. Although the sampling has been done at regular intervals, there may be time periods within the core when sedimentation rates were lower, thus, the 10 year gap

expected may actually reflect a 20 year gap and hence, the detail of every 10 years may not be seen within the record.

#### 4.5.2 Radiocarbon dating results

The results of the Radiocarbon dating are presented in table 4.3. This presents the sample sent for analysis, which are referenced relative to the samples within the core. The actual depth of the sample within the cores refers to the depth of the sample when viewed as one core, which is calculated using the equation outlined in section 3.1.1. The radiocarbon date, as quoted from the laboratories and the conventional radiocarbon date that is the radiocarbon date following corrections after the  $^{13}\text{C}/^{12}\text{C}$  analysis to ensure any isotopic fractionation in the sample is corrected. Finally the calibrated date is presented.

| Sample                     | Actual depth in the core (see section 3.1.1) | Radiocarbon date | $^{13}\text{C}/^{12}\text{C}$ Ratio | Conventional radiocarbon date | Calibrated ages (2 Sigma calibrated result)  |
|----------------------------|--|------------------|-------------------------------------|-------------------------------|--|
| HUM3 200 cm. (SUERC-2303). | 300 cm                                       | Not stated       | -29.7 ‰                             | 3439 +/- 25 BP                | 3486-3500 BP<br>3506-3524 BP<br>3555-3704 BP |
| HUM 3 82 cm (Beta-207757)  | 182 cm                                       | 3910 +/- 40 BP   | -26 ‰                               | 3890 +/- 40 BP                | 4420-4220 BP<br>4210-4170 BP                 |
| MAIVK 50 cm (Beta-208029)  | 66.18 cm                                     | 2750 +/- 40 BP   | -24.7 ‰                             | 2750 +/- 40 BP                | 2940-2770 BP                                 |

Table 4.3: Results from radiocarbon dating.

As table 4.3 indicates, the results of the radiocarbon dating show a reversal at the base of the core. This has implications for analysis and the construction of an age model. The possible causes for this switch and the implications for the study will be discussed in further detail in section 5.2.

#### 4.5.3 $^{210}\text{Pb}$ and $^{137}\text{Cs}$ dating

Subsamples were taken at every centimetre in the top 20 cm of the MAIVK core to prepare for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  dating. This was based upon a radiocarbon date of 3439  $^{14}\text{C}$  yrs BP at 300cm (the base of HUM3 core). Assuming a constant sedimentation rate from this point to the top of MAIVK core, provides a sedimentation rate of 11.8 years per cm. Although the sedimentation rate is unlikely to have remained constant throughout both cores, this provides a broad estimate of the sedimentation rate and

allows the number of samples required for  $^{210}\text{Pb}$  to be estimated. The upper limit for  $^{210}\text{Pb}$  dating is 200 years therefore, testing samples estimated to be older than this is not productive. Using this constant sedimentation rate model, 200  $^{14}\text{C}$  yrs BP is reached after 17 cm. It is likely that sedimentation rates have increased in the past 200 years and to take into account any compression within the core, the top 20 cm of the MAIVK core (=26.5 cm of the total core) was tested for  $^{210}\text{Pb}$  activity. The  $^{137}\text{Cs}$  peak in 1963 would be expected at approximately 40 yrs BP which is also well within the top 20 cm of the core.

#### 4.5.3.1 $^{210}\text{Pb}$ and $^{137}\text{Cs}$ results

The  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  results show no activity in any of the samples in the top 20 cm (see figure 4.9, 4.10 and appendix 3) therefore, the top of the core was dated using constant sedimentation rates calculated from the 3 radiocarbon dates. The possible reasons for the lack of activity are discussed in section 5.1.1.

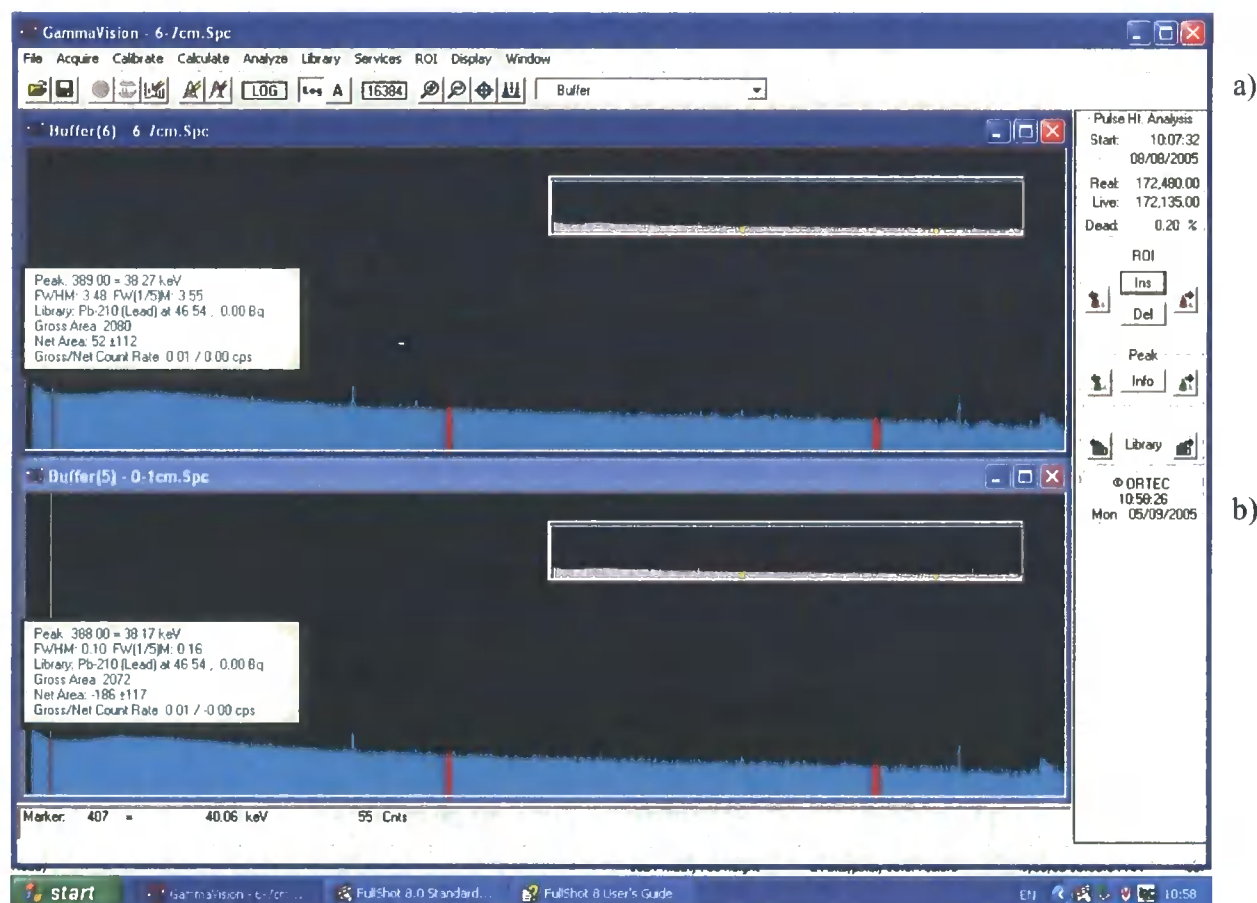


Figure 4.9:  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  results. a) MAIVK 6-7 cm; b) MAIVK 1-2 cm. The label on both the graphs indicates the position where  $^{210}\text{Pb}$  is detected. If  $^{210}\text{Pb}$  had been present

in the sample, a peak would be present at this point and the amount of  $^{210}\text{Pb}$  in the sample is calculated from the net area.

Figure 4.9a (MAIVK 6-7cm), the  $^{210}\text{Pb}$  count is  $52 \pm 112$ . As the error on this is greater than the actual count, the activity in the sample is below background levels.

Figure 4.9b (MAIVK 1-2cm) displays similar characteristics. The  $^{210}\text{Pb}$  count is  $-186 \pm 117$ . As this is the top sample, this should display the greatest amount of  $^{210}\text{Pb}$  as it is the most recent sediment however, this is not the case and hence, the sediment cannot be dated using these results. The red band on both graphs nearest to the  $^{210}\text{Pb}$  peak indicates where the  $^{137}\text{Cs}$  peak would be if there was any activity in the sample (see figure 4.10).

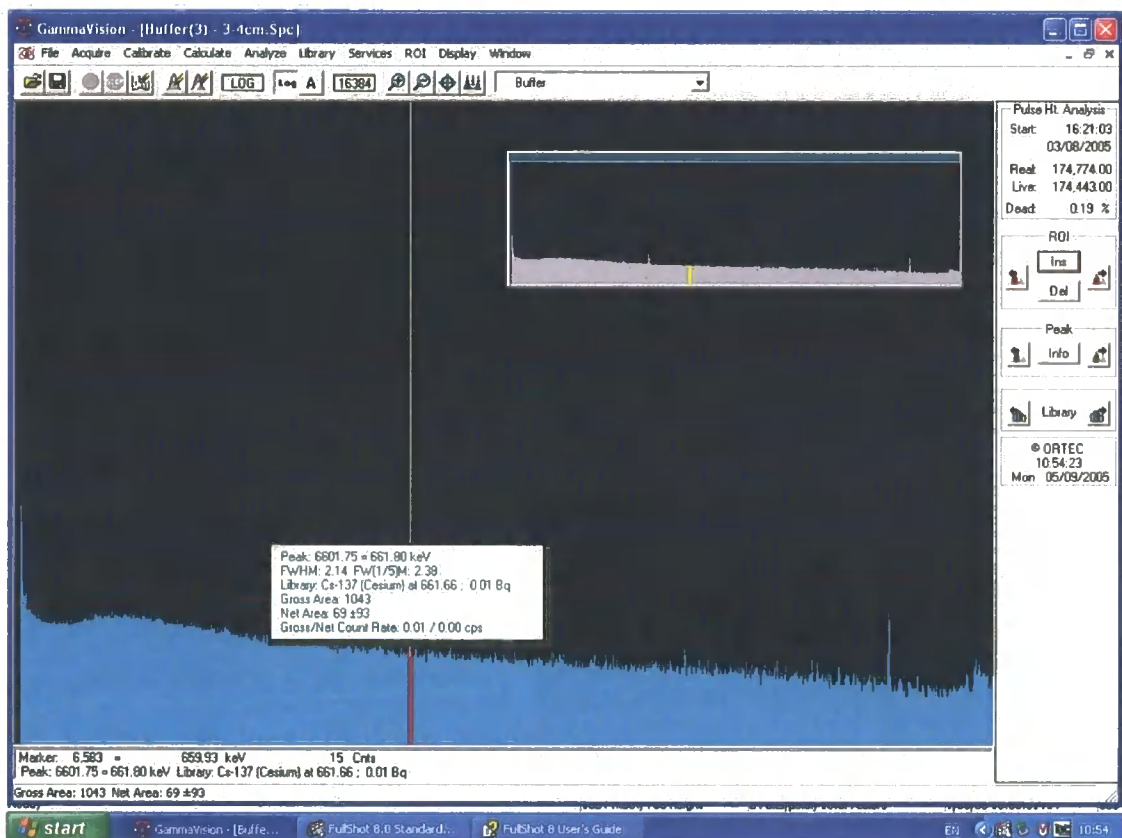


Figure 4.10:  $^{137}\text{Cs}$  results (MAIVK 3-4 cm). The label on the graph indicates the position of a peak if there was any  $^{137}\text{Cs}$  in the sample. The label indicates that in this sample, the amount of  $^{137}\text{Cs}$  is  $69 \pm 93$ ; therefore there is no  $^{137}\text{Cs}$  in the sample beyond background levels. Each sample tested displayed similar characteristics and therefore this method cannot be used to date these samples.

#### 4.6 Summary

This chapter only describes the results; results will be analysed further in the following chapters. Chapter 5 will carefully examine the results and discuss the implications these results have for each objective as outlined in chapter 1.

## Chapter 5

### Discussion



Plate 5: Fur seals at South Georgia

## 5: Discussion

Before discussing the interpretation of the fur seal hair and geochemical results, a robust age model will be established from the Radiocarbon dates and the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  results and used as a basis for analysis.

### 5.1 Age Model

From the results of the radiocarbon dates, it is essential to establish an age model on which to compare the fur seal hair abundance changes and hence, fluctuations can be correlated to climate change. As the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  results were inaccurate, these cannot be used.

As table 5.1 shows, the radiocarbon dates show an apparent reversal at the base of the core. As this is not possible, it is likely that one of the dates is inaccurate and cannot be used. The following section discusses the implications for using each of the radiocarbon dates and the likelihood of its accuracy. Table 5.1 presents the different age models and the implications these models have for analysis.

|                | HUM 3 200cm<br>(SUERC - 2303) | HUM 3 83cm<br>(Beta -207757) | MAIVK 50cm<br>(Beta 208029) | Basal date ( $^{14}\text{C}$<br>years BP) | Sedimentation Rate<br>(cm/yr) |                  |
|----------------|-------------------------------|------------------------------|-----------------------------|---|-------------------------------|------------------|
|                |                               |                              |                             |   | Lower<br>section              | Upper<br>section |
|                | 3439                          | 3910                         | 2750                        |   |                               |                  |
| <b>Model 1</b> | ♦                             |                              |                             | 3439                                      | 0.087                         |                  |
| <b>Model 2</b> |                               | ♦                            |                             | 6412                                      | 0.048                         |                  |
| <b>Model 3</b> |                               |                              | ♦                           | 12466                                     | 0.024                         |                  |
| <b>Model 4</b> |                               | ♦                            | ♦                           | 5051                                      | 0.10                          | 0.024            |
| <b>Model 5</b> | ♦                             |                              | ♦                           | 3439                                      | 0.34                          | 0.024            |

Table 5.1 – Different age models and the implications this has for sedimentation rate and basal date in the core.

#### 5.1.1 Model 1 (3439 $^{14}\text{C}$ yrs BP only)

As table 5.1 shows, if only the basal date was used to date the core, this would give a constant sedimentation rate of 0.087cm/yr throughout the core. This is unlikely to be the case due to the climatic changes documented in the catchment through the past 3439  $^{14}\text{C}$

yrs BP (see figure 2.11). Although this is possible, as there are other dates available, using an additional date to enhance the accuracy is more favourable.

#### 5.1.2 Model 2 – (3910 $^{14}\text{C}$ yrs BP only)

Assuming the radiocarbon date from 187cm is correct; this would imply that the basal date is inaccurate. Using this date as table 5.1 indicates, the basal date would be 6412  $^{14}\text{C}$  yrs BP and the sedimentation rate would be 0.048 cm/ yr throughout the core. Using an additional date is favourable as this provides an enhanced accuracy and prevents the sedimentation rate been assumed from one constraining point. As a consequence of these factors, this model will not be used.

#### 5.1.3 Model 3 – (2750 $^{14}\text{C}$ yrs BP)

Using the radiocarbon date from the MAIVK core at 50 cm gives a very low sedimentation rate for the entire core and would imply that the core provided a record for the past 12466  $^{14}\text{C}$  yrs BP. Given past climate reconstructions for this period, it is thought that the catchment was still glaciated in 12466  $^{14}\text{C}$  yrs BP. From analysis of the core stratigraphy (see section 4.1) and climate reconstructions from similar lakes in the Maiviken area, it can be inferred that the lake catchment formed following deglaciation (Clapperton et al 1989). Using this theory, it is thought that this model is inaccurate and will not be used.

#### 5.1.4 Model 4 – 3910 $^{14}\text{C}$ yrs BP and 2750 $^{14}\text{C}$ yrs BP

This model uses two radiocarbon dates to enhance the accuracy of the model. Using the dates from HUM3 82 and MAIVK 50cm implies the core provides a record for the past 5051  $^{14}\text{C}$  yrs BP.

The basal date HUM3 (200cm) (SUERC -2303) is thought to be reliable as it has been radiocarbon dated in two separate laboratories (SUERC and Prozan), each giving a very similar date (Moreton *et al.* unpublished data). If this date is correct, the HUM 3 (82cm) date is thought to be accurate and therefore, this model will not be used.

### 5.1.5 Model 5 – 3439 <sup>14</sup>C yrs BP and 2750 <sup>14</sup>C yrs BP

As the basal date HUM3 (200cm) has been dated twice by different laboratories, both giving a similar date, it is thought that this date is accurate and hence, it can be inferred that the date obtained at HUM 3 (83cm) is inaccurate and will not be considered in analysis. The use of two radiocarbon dates aids in reducing error in the age model hence, the date obtained from MAIVIK (50cm) will also be used in the model.

### 5.1.6 Calculating the age model

The sedimentation rate was calculated using the basal date from HUM3 200 cm and the date obtained from MAIVK 50 cm using equation 5.1. Before calculating any dates, the samples were converted into depths as described in section 3.1.1 (equation 3.1).

(no. of years the sediment section covers) / (no. of cm covered x depth of the sample)

Equation 5.1: date for each sample in the core

Lower section of the core (66.18-300 cm)

$$\begin{aligned} &= (3439-2750) / (300-66.18) \\ &= 2.946 \text{ years represented by each cm of sediment} \\ &= \text{sedimentation rate } 0.34 \text{ cm/year} \end{aligned}$$

Upper section of the core (0-66.18 cm)

$$\begin{aligned} &= 2750 / 66.18 \\ &= 41.56 \text{ years represented by each cm of sediment} \\ &= \text{sedimentation rate } 0.024 \text{ cm/ year} \end{aligned}$$

The top of the core cannot be accurately dated due to the problem in <sup>210</sup>Pb and <sup>137</sup>Cs dating. Although samples for radiocarbon dates were selected from relatively equal depths down the core, due to the age of the youngest date at the top of the core the sampling resolution is not time stratigraphic. However, this problem cannot be alleviated without dating an additional sample nearer the top of the core. Although it is unlikely that the sedimentation rate has been constant in the catchment since 2750 <sup>14</sup>C

yrs BP, as the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  results were unsuccessful, this is the only estimate available.

## 5.2 Dating inaccuracies

The possible reasons for the inaccuracies in the dating techniques are outlined in the following sections.

### 5.2.1 $^{210}\text{Pb}$ problems

The results of the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  show no activity above background levels, therefore, this method cannot be used as a means to date the top of the core (see figures 4.9; 4.10). The date for the top of the core has therefore, been estimated to be zero. A constant sedimentation rate assumed to the  $^{14}\text{C}$  date at 66.18 cm depth (MAIVK 50 cm) has been used to date the top section of the core.

Although the sub Antarctic region is not an area commonly recognised as having  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  dating problems, there have been no published studies on South Georgia that have successfully dated lake sediments using  $^{210}\text{Pb}$ . The apparent lack of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  is difficult to explain, however, possible reasons for this are outlined below and include the loss of the sediment-water interface, catchment characteristics, detection limits and location of the study site.

#### 5.2.1.1 Loss of the sediment water interface

It is possible that the sediment analysed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  is not the true core top (i.e. sediment-water interface at the time of extraction). If this is the case, the sediment that appears to be at the top of the core will be older than 200 years BP and hence, all of the  $^{210}\text{Pb}$  in the sample is likely to have already decayed. Although this is feasible, it would require a minimum of 4 cm from the top of the core to be lost (calculated on constant sedimentation rate discussed in section 5.1.6). The use of a Kullenberg corer for the top section of the core was designed to prevent the loss of the core top, it is possible that the top 4cm of the sediment in the lake was lost during coring as sludge at the top of the core.

Despite these complications, the dating model suggests the sedimentation rate in the core has been constant for the past 2750  $^{14}\text{C}$  yrs BP. Although this is the best estimate

available with the data, it is unlikely that this is the case. As figure 2.11 indicates, the climate has changed significantly during this period and today the climate is warmer than at 2750  $^{14}\text{C}$  yrs BP hence, the sedimentation rates would be expected to be higher. Coupling this with the compaction of deeper sediment, causes the  $^{210}\text{Pb}$  to be present in samples deeper than 4 cm. As a consequence, all the  $^{210}\text{Pb}$  would not be lost in the sediment water interface and all the  $^{210}\text{Pb}$  in the core would not have decayed. The peak of  $^{137}\text{Cs}$  in the sediment, used as a reference point for the  $^{210}\text{Pb}$  dating occurs in 1963 hence, if all the  $^{210}\text{Pb}$  is depleted, it is not surprising that the peak in  $^{137}\text{Cs}$  has also been lost.

#### 5.2.1.2 Catchment Characteristics

The catchment of the lake may not be conducive to the accumulation of  $^{210}\text{Pb}$  fallout. It is widely recognised in the Antarctic region, the strongest  $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  signals are found in large catchments which experience a focussing effect (Hodgson *et al.* 2004). As section 2.2.3 and 2.2.5 discuss, the catchment is small and very localised hence, decreasing the likelihood of any  $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  accumulation.

As Appleby *et al.* (1995) suggest, the  $^{210}\text{Pb}$  flux from the atmosphere varies globally and the fallout to Antarctica is sparse. Hardy *et al.* (1973) further establish that the  $^{137}\text{Cs}$  fallout in Antarctica is a magnitude lower than fallout rates in mid latitudes of the Northern Hemisphere. Doran *et al.*'s. (1999) study in a lake in the McMurdo Dry Valleys, Antarctica, indicates that levels of  $^{210}\text{Pb}$  were high in some samples however, counts were not sufficient in all samples to allow an age chronology to be formulated. It was concluded that the perennial ice cover of the lake retarded the deposition of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in lake sediments (Doran *et al.* 1999). This coupled with low fall out rates of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in Antarctica prevented the accumulation of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the lake reaching levels above background.

Humic lake is ice covered for 4-5 months of the year and as discussed in section 2.2.5 ice cover limits lake inputs hence, the pathways for  $^{210}\text{Pb}$  reaching the water column are restricted (Doran *et al.* 1999). The accumulation of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the sediment may therefore, be limited to only some months of the year and result in the accumulation of very low levels of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  that are not significantly above background levels and therefore cannot be detected.

Although there have been numerous studies of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in Antarctica which suggest that the fallout is lower than other regions, many studies have yielded sufficient concentrations to allow an accurate chronology to be calculated (Jones and Juggins 1995; Roberts *et al.* 2004). Catchments on Signy Island which experience a similar climate to South Georgia, have yielded  $^{210}\text{Pb}$  results and allowed a  $^{210}\text{Pb}$  chronology to be determined (Jones and Juggins 1995; Noon *et al.* 2001; Jones *et al.* 2000). These catchments experience ice cover for 8-11 months of the year and are influenced by a large population of fur seals (Noon *et al.* 2001) indicating that it is not the seasonal ice cover or the influx of fur seals that is limiting the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the catchment.

#### 5.2.1.3 Detection Limits

The sample size used in detection was only 0.30g, compared to the recommended 1g. This was due to the limited sample available. As the fallout rates of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in Antarctica are limited, this coupled with a small sample size may have resulted in any  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the sample being below background levels and detection limits. Analysing more sample in the detectors may reduce this problem, however, the scope of this study did not allow this.

#### 5.2.1.4 Location of the study site

Previous attempts to obtain a  $^{210}\text{Pb}$  chronology at South Georgia have proved problematic and there are no published accounts of a successful  $^{210}\text{Pb}$  chronology at South Georgia (Rosqvist, G. pers. comm.). This suggests that the lack of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in lake sediments is a characteristic of the island rather than a result of unfavourable specific catchment characteristics or the loss of sediment during extraction.

Ku and Lin (1976) establish from studies across the Antarctic Convergence that concentrations of  $^{210}\text{Pb}$  south of the Antarctic Convergence increased to 18 dpm/100kg (disintegrations per minute/ 100 kg) from 8dpm/100kg in waters to the north of the Antarctic Convergence. The Weddell Sea region of the Southern Ocean is particularly high in  $^{210}\text{Pb}$  waters, especially on the northern and western flanks of the gyre (Farley and Turekain 1990). As South Georgia is located on the north west flank of this gyre (see figure 2.2), the large oceanic flux of  $^{210}\text{Pb}$  will influence the accumulation of  $^{210}\text{Pb}$  in the fur seals and hence, the terrestrial accumulation of  $^{210}\text{Pb}$  on South Georgia. However, as Shimmield *et al.* (1995) establish, in the Bellingshausen Sea, Antarctica

although recorded  $^{210}\text{Pb}$  activity is similar to other areas (e.g. the north east Atlantic), there is virtually no atmospheric input of  $^{210}\text{Pb}$ . While the Weddell Sea surrounding South Georgia is abundant in  $^{210}\text{Pb}$  it is possible that the source of the  $^{210}\text{Pb}$  is atmospheric and as a consequence, terrestrial pathways for the  $^{210}\text{Pb}$  are limited. If this is the case, sediment records will be depleted in  $^{210}\text{Pb}$ .

#### 5.2.1.5 Summary of $^{210}\text{Pb}$ problems

Without further research into the accuracy of the  $^{210}\text{Pb}$  detector, the potential limitations of the small sample size and the low atmospheric  $^{210}\text{Pb}$  flux at South Georgia, it is difficult to determine the cause of the low  $^{210}\text{Pb}$  concentration in the sediment.

From the evidence available, the most plausible explanation is a combination of the small sample size, the accuracy of the detector and the location of South Georgia relative to the atmospheric flux of  $^{210}\text{Pb}$ . While it is possible that the top section of the core has been lost, the catchment characteristics are not conducive to  $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  accumulation and the sample size was inadequate. As there are no studies on South Georgia that have found sufficient  $^{210}\text{Pb}$  to provide an age chronology, this would suggest that the factor(s) affecting this lack of  $^{210}\text{Pb}$  are regional and not localised to the catchment or the core used in this study.

In this study, the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  do not provide a core top chronology and so the top of the core is assumed to be 0 years, with a constant sedimentation rate from 0 cm to the  $^{14}\text{C}$  date at 66.18 cm (MAIVK 50cm).

#### 5.2.2 Radiocarbon problems

The three radiocarbon dates are not in age stratigraphic order (see table 4.3). Specifically, the radiocarbon dates suggest a reversal at the base of the core of 451 years (see figure 5.1); therefore, the middle date obtained from sample HUM3 82-83cm was not used in the age model. Possible reasons for this reversal are outlined below.

##### 5.2.2.1 Seal influence

Radiocarbon dating of the surface sediment in the lake has shown that the sediment at the sediment-water interface has an apparent age of  $426 \pm 37$   $^{14}\text{C}$  years BP (Moreton *et*

*al.* unpublished data). Surface sediments with an apparent age are generally only found in marine systems and this ageing of the surface sediment is known as the marine reservoir effect. It is not commonly found in freshwater systems such as Humic lake, however, it is possible that the apparent age of the sediments in Humic Lake may be a consequence of the abundance of seals in the catchment and the influence of marine derived faecal material on the sediments. Such an effect has been found previously in freshwater lakes in catchments abundant in penguins (Björck *et al.* 1991a; Zale and Karlen 1989).

It is widely recognised that sea water has a non-zero radiocarbon age: surface water sinks to intermediate and depths without any further replenishment of  $^{14}\text{C}$  (Walker 2005). Fur seals and (penguins) feed predominantly off krill, which live in oceanic areas depleted in  $^{14}\text{C}$ . Krill in the Weddell Sea have an apparent  $^{14}\text{C}$  age of  $810 \pm 120$   $^{14}\text{C}$  years, therefore, the absorption of the old  $^{14}\text{C}$  by the fur seal consequently gives the fur seal an apparent age (Gordon and Harkness 1992). Fur seal excrement and hair washed into the lake contain this similar level of  $^{14}\text{C}$ , which dilute the level of  $^{14}\text{C}$  in the lake sediment, therefore, when sediment is radiocarbon dated it has an apparent age. In a previous study Moreton *et al.* (unpublished data) found this ageing effect to be 426 years.

As the ageing effect is caused by fur seal influence, the magnitude will vary depending upon the size of the fur seal population (and penguins if present). As the fur seal population has varied throughout the Holocene, the apparent age at the core top is unlikely to have been constant through the Holocene. As a consequence, the age of deeper sediment cannot be corrected by the same factor as the sediment surface.

The two dates experiencing the age reversal are located at 183 cm ( $3910 \pm 40$  BP) and 300 cm ( $3439 \pm 25$  BP). Assuming the radiocarbon date at 183 cm *has* been affected by this marine reservoir effect and the basal date (300 cm) has not, due to the difference in fur seal hair abundance, (fur seal hair abundance is significantly higher at 183 cm compared to 300 cm) correcting the date obtained from 183 cm yields a date of  $3464$   $^{14}\text{C}$  yrs BP, which is almost identical to the basal date. However, there is 117cm of sediment separating these two dates hence, this sedimentation rate is unrealistic. Furthermore, the correction factor of 426 years is derived from the top of the core; as figure 4.1 shows, fur seal hair abundance is 3.5 times greater at the top of the core than at 183cm. It can

be inferred that the fur seal population at 183 cm was only 33% that at the top of the core and so the correction factor is likely to be significantly less at 183cm than at the core top. Taking this into account and a correction for the basal date, the date at 183cm is still older than the basal date. Hence, although the seal influence is a possible factor ageing the date, it cannot be used to fully explain the ageing of the sample.

#### 5.2.2.2 Contamination

Radiocarbon dating depends upon the decay of the  $^{14}\text{C}$  in the sediment, however, it assumes that all the material incorporated in the sediment is 'new' carbon (Walker 2005). Yet, it is possible that older material such as soil sediment or weathered carbon bearing rocks could be washed into the lake and incorporated into the sediment (Lowe and Walker 1997; Hodgson *et al.* 2004). This contaminates the  $^{14}\text{C}$  in the sediment with older  $^{14}\text{C}$  therefore, the date of the sediment appears older than it actually is. Alternatively, reworking of the sediment once deposited may result in older sediment lying above younger sediment causing in a reversal.

As Björck *et al.* (1991c) indicate, snow and ice contain old  $\text{CO}_2$  therefore, if this melts in the catchment it can result in the input of older carbon into the lake. As vegetation grows in the lake it incorporates the older carbon. When such vegetation dies, this carbon is incorporated into the sediment, producing a  $^{14}\text{C}$  content significantly lower than the modern day  $^{14}\text{C}$  concentrations hence, the date of the sample appears older. As contamination alters the age of the sediment, it is difficult to correlate this section of the core with climate changes which would help determine a potential climate change in the catchment at this time that may have caused an influx of sediment. From the age model outlined in section 5.1, 183 cm is dated at approximately 3000  $^{14}\text{C}$  yrs BP. Assuming the date is correct, correlating this with climate changes on South Georgia (see figure 2.14), at 3000  $^{14}\text{C}$  yrs BP, the climate was thought to be dry and warm, with no evidence of any glacial activity therefore, it is unlikely that snow and ice cover caused an influx of old  $^{14}\text{C}$  which consequently aged the sediment.

#### 5.2.2.3 Ice cover

It is widely documented that if the ice cover on a lake reaches the basal sediments, this can cause sediment disturbance. Although this process is only common in lakes up to 2 metres deep, as the lake in the study is 3.5 metres deep, this is not affecting the basal sediments today. During the Late Holocene, the climate has been colder than today and

ice cover has been more extensive (see figure 2.11). Although proxy climate records suggest that the catchment has not been influenced by glacial activity, it is possible that the climate cooled sufficiently to cause the lake to freeze to a greater depth. If this was the case, it is possible that during the past 3439  $^{14}\text{C}$  yrs the base of the lake has been frozen causing the reworking of the sediments.

As discussed in section 4.1, as the core stratigraphy shows homogenous sediment through the majority of the core, there is no indication of sediment reworking following deposition.

#### 5.2.2.4 Summary

As the bulk sediment sample was dated, the most plausible explanation for the reversal of ages at the base of the core is the incorporation of older carbon as a result of sediment reworking or the influx of older carbon from the catchment. Using the age model to determine the climate at the time this layer of sediment was deposited, the climate appears relatively warm and dry, hence, sedimentation is unlikely to have been disrupted. However, the reason for using this sample was due to the dramatic change in the geochemical record at this point. This dramatic change would suggest that a significant shift took place in the catchment at this point, therefore, may have disrupted the sediment or caused an inwashing of older sediment, and caused a change in the  $^{14}\text{C}$  ratio. Coupled with the marine reservoir effect caused by the increase in fur seals (as discussed in section 5.2.2.1), may give the sediment an apparent age, hence, the sediment appears older than the actual age it was deposited. If the samples were to be dated again, to alleviate this issue wood and plant fragments could be extracted and dated separately to determine the aging effect this 'old' carbon may have upon the sample.

#### 5.2.3 Implications for the study

The age model as outlined in section 5.1 uses 2 radiocarbon dates to infer constant sedimentation rate through the core. This has resulted in a significant change in sampling resolution between the lower section of the core (6 yrs) and the upper section of the core (110 yrs) (see figure 5.1). At the base of the core, as the sedimentation rate is 0.34cm/year, the resolution is high at  $\sim 6$  years. The sedimentation rate in the top section of the core is 0.024cm/ year and therefore, the sampling resolution is

significantly lower at  $\sim 110$  years. Although the core top is unlikely to experience such a low sedimentation rate, as the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  dating was unsuccessful, this is the best estimate available. This however has implications for analysis; if the reason for the lack of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the top samples of the core is a result of loss in the sediment-water interface, recent 20<sup>th</sup> and 21<sup>st</sup> century changes in the fur seal population are not represented in this core. Assuming the core top (0 cm) is the present day, (as the Kullenberg corer was used to ensure the sediment-water interface remained in tact) the poor resolution at the top of the core prevents 20<sup>th</sup> century changes being fully evaluated as the sampling resolution (110 years) covers the entire 20<sup>th</sup> century change in the population.

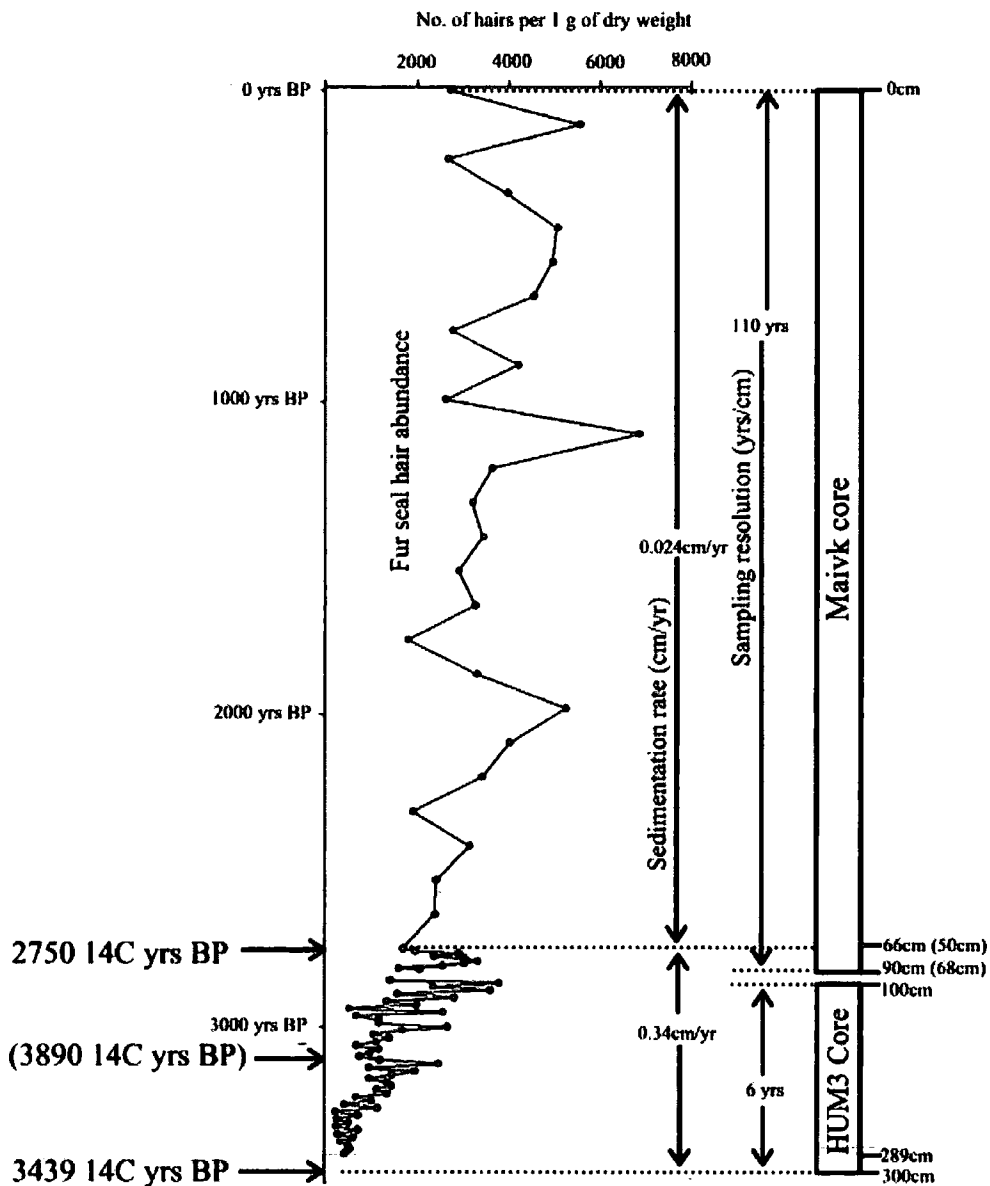


Figure 5.1: Sedimentation rates in the core relative to core position, radiocarbon dates and sampling resolution.

Figure 5.2 highlights the effect the change in sedimentation rate has on the results and the observed trend in fur seal hair abundance fluctuations. Plotting the fur seal hair abundance against the age scale skews the data and causes the step changes at the base of the core to be more pronounced. At the top of the core, due to the reduced sampling resolution relative to age, the increase in fur seal hairs observed in the depth record is not as distinct.

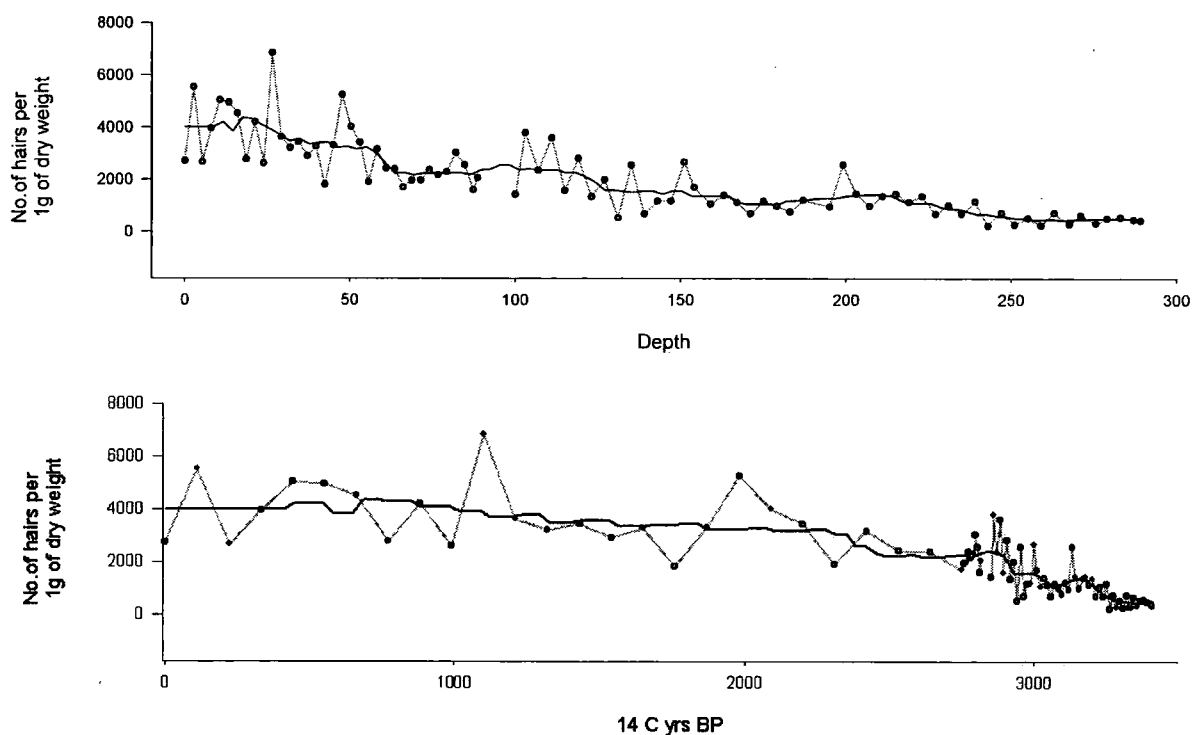


Figure 5.2: a) Fur seal hair abundance relative to depth in the core. b) Fur seal hair abundance relative to time (as calculated using the age model outlined in section 5.1.6).

As the time - stratigraphic resolution in the upper core is significantly lower than the lower core, in this section, the averaging function has averaged a range of points covering a larger time scale than in the lower core. As shown in figure 5.1, the sampling resolution is 110 years therefore, a running average of 0.1 is equal to an average of ~800 years, thus, when considering the top section of the core, I will refer to the raw data rather than the running average. Even referring to the raw data, the sampling resolution is too low to fully assess the changes in fur seal populations in the past 200 yrs BP. For this reason, the changes in fur seal hair abundance relative to specific climate events cannot be evaluated.

### 5.3 Assumptions

Before analysing the results, due to the issues relating to dating the core, a number of assumptions must be made. As outlined by Hodgson *et al.* (1998), fur seal hair abundance has been used as a proxy for fur seal populations. This is based upon the assumption that the rate of hair deposition relative to the fur seal population has been constant through the entire core. As outlined in section 2.3.2, the climate of the Humic lake catchment has changed throughout the core and as discussed affect the inputs into the lake. As a consequence, this will impact upon the rate at which fur seal hairs are entrained in the sediment and deposited in the lake. For example, during periods of increased ice cover, inputs into the lake are reduced; following the melt of ice, the inputs would increase hence, increasing the flux of hairs into the lake. As a consequence of this, the number of fur seal hairs relative to the number of fur seal in the catchment may not have been consistent throughout the core. Furthermore, lake circulation may have altered, reducing the retention of the hairs within the lake sediments. For example, in section 3.3 the hairs are described as being incorporated in organic material and hence, making extraction difficult. During periods of reduced organic lake content it is possible that the sediment does not retain the hairs in the same manner as during increased organic content, thus, the deposition of hairs relative to the fur seal population is not constant through the core. The extent to which this has occurred is difficult to quantify, therefore, for the purpose of this study it is assumed that the fur seal hair abundance relative to the fur seal population is constant through the core.

### 5.4 Late Holocene changes in fur seal populations

As outlined in the objectives, the fur seal population can be reconstructed using fur seal hair abundance and geochemistry. I will firstly evaluate the results of the fur seal hair abundance method followed by the geochemical analysis. For the purpose of this study, following Hodgson *et al.* (1998) and Sun *et al.* (2004), it is assumed that fur seal hair abundance is directly proportional to the size of the fur seal population and hence, provides a proxy record of the fur seal population.

#### 5.4.1 Fur seal hair abundance

Figure 5.3 shows the fur seal hair abundance plotted using the age model described in section 5.1. As the sedimentation rate has changed from 0.34cm/year in the lower

section of the core to 0.024cm/ year in the upper section of the core, the resolution of the hairs is lower at the top of the core

As shown in figure 5.3, fur seal hair abundance in Humic lake has gradually increased through the late Holocene from at least 3439  $^{14}\text{C}$  yr BP. The most dramatic increases in the hair abundance occurs from 3300-3200  $^{14}\text{C}$  yr BP and 3000-2800  $^{14}\text{C}$  yr BP as the number of hairs per 1g of dry weight of sediment increases by a factor of 2.8. A third significant increase is observed from 2600  $^{14}\text{C}$  yrs BP as the hair abundance increases by a factor of 1.3 in 220 years. From 2400  $^{14}\text{C}$  BP, hair abundance increases gradually to the top of the core. Figure 5.3b indicates that the fur seal hair abundance has been constant for the past 500 years however, from the census data (see figure 2.17), it is clear that this is not the case. This inaccuracy is primarily due to the low sampling resolution at the top of the core.

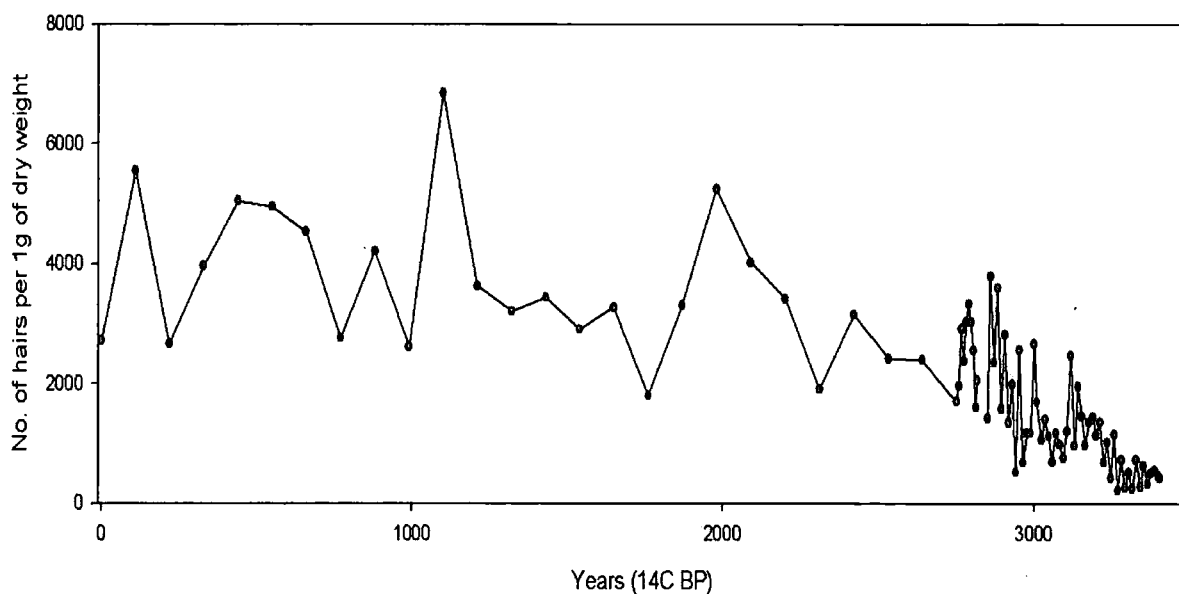


Figure 5.3a: Fur seal hair abundance fluctuations at South Georgia for the past 3439  $^{14}\text{C}$  years BP.

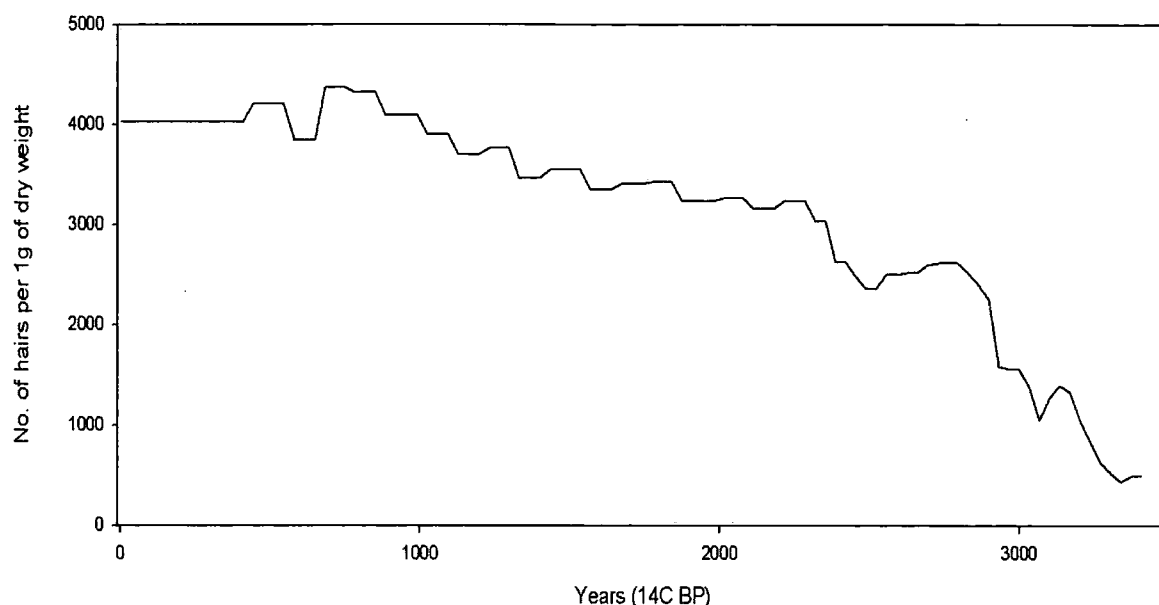


Figure 5.3b: Average fur seal hair abundance for the past 3439  $^{14}\text{C}$  years BP. The average was calculated on Sigma Plot using running average function, sampling proportion set at 0.1.

The most significant increase in fur seal hair abundance occurs at the base of the core as hair abundance increase almost 10 fold, from 268 hairs per 1g of dry weight to 2575 hairs per 1g of dry weight in a period of 150 years (3294-3141  $^{14}\text{C}$  yrs BP). Further peaks in the hair abundance occur at 2000  $^{14}\text{C}$  yrs BP and 1100  $^{14}\text{C}$  yrs BP. The fur seal population increases by a factor of 2.8 in 300  $^{14}\text{C}$  years to peak at 2000  $^{14}\text{C}$  yrs BP and declines by a similar factor in only 200  $^{14}\text{C}$  years. This rapid increase and decrease, prior to human intervention suggests that the fur seal population has the capacity to fluctuate significantly (potentially doubling/halving) as a result of natural causes. An increase in hair abundance of a similar magnitude is observed at 1100  $^{14}\text{C}$  years, suggesting that the population increased by more than 100% in 100 years and subsequently declined in a similar period of time. More recently from 700  $^{14}\text{C}$  yrs BP, hair abundance increased by a factor of 1.8, to a peak at 400  $^{14}\text{C}$  yrs BP. From this peak, hair abundance declined by a similar magnitude to a minimum at 200  $^{14}\text{C}$  yrs BP.

Although hair abundance fluctuates through the core, significant increases in the hair are not sustained once a threshold of 3000 hairs per 1 g of dry weight is attained. At the base of the core (3439-2900  $^{14}\text{C}$  yrs BP) hair abundance is below 3000 hairs therefore, the increases are sustained and the record does not indicate any declines. Although the

abundance does increase beyond 3000 hairs per 1 g of dry weight, to a maximum of almost 7000 hairs per 1 g of dry weight, this higher abundance in fur seal hair cannot be sustained for periods longer than c. 200  $^{14}\text{C}$  yrs BP before hair abundance dramatically declines. This suggests that once the fur seal population reaches a certain level it cannot be sustained and results in a (dramatic) decline, implying that the population has been highly variable.

During the past 2600  $^{14}\text{C}$  yrs BP there does not appear to be any factor that has caused fur seal hair abundance to decline below 2000 hairs per 1g of dry weight. This suggests that within the last 2600 years the population has not changed by more than a factor of 3.5 despite the population increasing from a minimum at the base of the core (3439  $^{14}\text{C}$  yrs BP).

#### 5.4.2 Geochemical record

As discussed in section 3.4, geochemistry has been used previously to reconstruct fur seal populations and it is expected that concentrations of similar elements will correlate with fur seal and penguin populations as krill is their primary prey. However, the chemical processes in each animal may differ, hence, it is possible that alternative mechanisms may influence the concentrations of elements to a greater extent than fur seals. In addition to this, it must be noted that fur seals are not the sole species influencing the geochemical signature on South Georgia. For example, although penguin populations at the study site are not dominant today, it is possible that penguin populations were more extensive during the late Holocene and therefore, influenced the geochemistry of the catchment (Zale 1994). Other possible influences on the geochemistry are the climate signature and the pressure of weathering on the catchment. As the climate has fluctuated through the core, the climate influence on the geochemistry is unlikely to be constant through the core and therefore, it is possible that the fur seal signature may be obscured by this climate influence.

For the purpose of this study, as the exact signature of these other influences is unknown, it is assumed that any correlation in geochemistry and fur seal hair abundance could be an indirect link to the fur seal population. A difference in results between this study and Sun *et al*'s (2004a) study may be explained by the difference in catchment characteristics and lake composition. Taking these factors into account, I will assess

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whether the geochemical record is an indicator for fur seal presence and hence, used as proxy for fur seal populations at South Georgia.

#### 5.4.2.1 Group A (Carbon, Nitrogen, Strontium, Aluminium)

The elements in group A do not fluctuate significantly with the fur seal population (see figure 5.4). Although previous studies have highlighted that carbon and nitrogen fluctuate with fur seal and penguin activity (Sun *et al.* 2004a), this does not appear to be the case at South Georgia. As these studies were done on different islands, the differing catchment characteristics may influence the initial concentration of elements and therefore, the point of saturation will alter.

The correlation in previous studies does not necessarily imply causation. Sun *et al.* (2004a) correlate the fur seal population changes with climate changes and so the catchment characteristics will also change hence, influencing element concentrations. Although in Sun *et al.*'s (2004a) study, the fur seal population is changing in response to climate changes, it is possible that the element concentrations are changing in response to climate changes, rather than changes in the fur seal population. On South Georgia, although the fur seal population may influence the element concentrations, alternative mechanisms such as an ecosystem change may be altering the element concentrations.

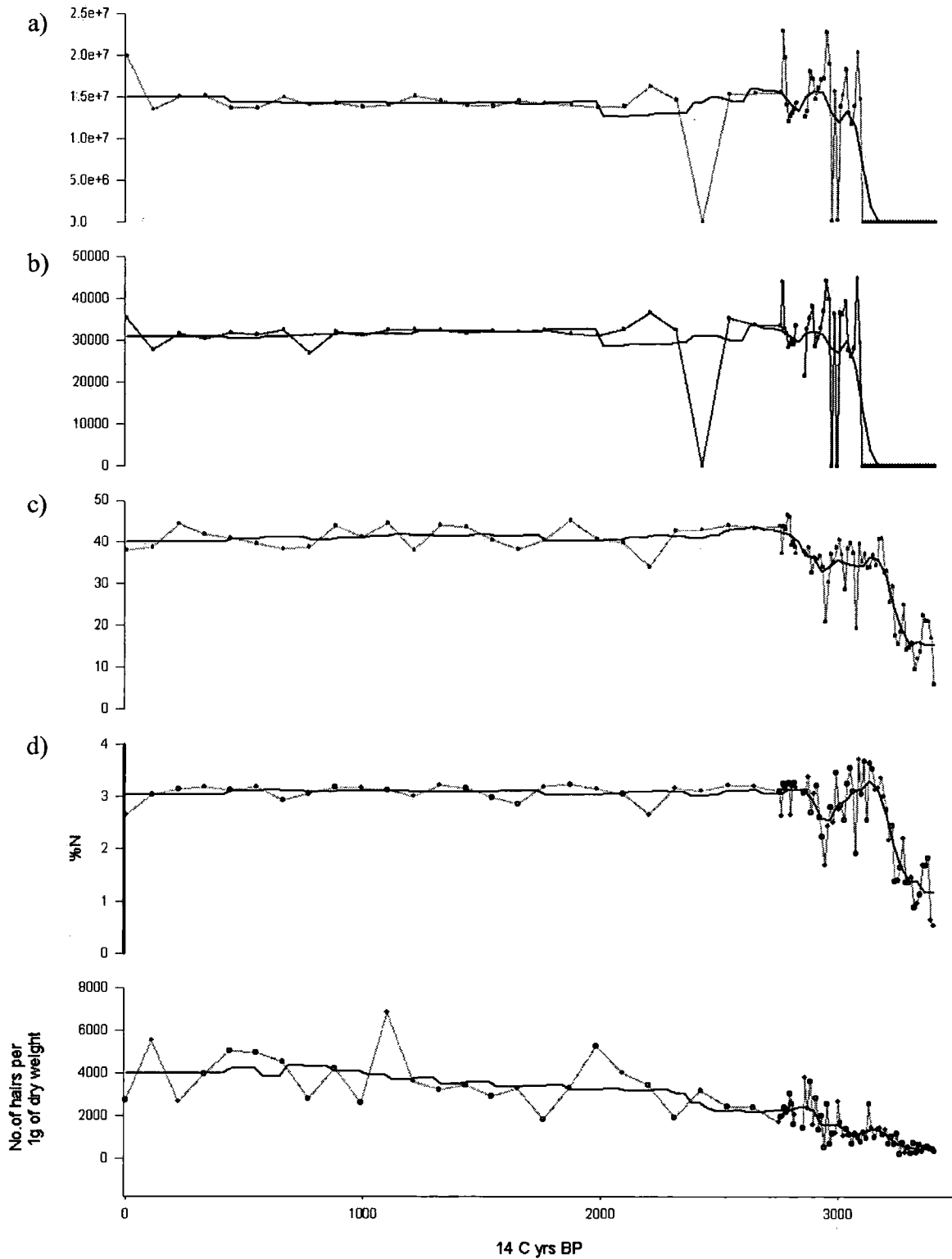


Figure 5.4: Element concentrations of group A compared to fur seal hair abundance relative to age. a) Nitrogen; b) Carbon; c) Strontium d) Aluminium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 5.4.2.2 Group B (Potassium, Titanium, Barium, 57-Iron, Sodium)

These elements do not reflect the fur seal hair abundance and therefore, cannot be used as bio indicators for fur seal populations (see figure 5.5). None of the elements have been used successfully as bio indicators previously, a point reinforced by this study. The only element thought to be a possible indicator of fur seal abundance was sodium due to its high concentration in seawater therefore, likely to show high concentrations in krill and fur seals. However, as sodium also increases with weathering, the association of sodium with the other element concentrations in this group suggests that in this catchment, concentrations of sodium are more closely associated with weathering than with fur seals.

#### 5.4.2.3 Group C (Copper, Zinc, Cadmium, Lithium)

Significant increases in the concentration of these elements correlates with the rapid increase in fur seal hair abundance at 3100  $^{14}\text{C}$  yrs BP and 2800  $^{14}\text{C}$  yrs BP, with a lag of approximately 100 years (see figure 5.6). Copper concentrations only increase for a period of 100 years before declining back to the initial concentration. This is not observed in the fur seal hair abundance record however, after the increase at 3000  $^{14}\text{C}$  yrs BP, the fur seal hair abundance declines slightly and remains at this lower level for 100 years. It is possible that copper is a bio indicator of fur seal presence but only once a threshold of 1500 hairs per 1g of dry weight is exceeded. Below this level, the fur seal population is not significant enough to influence the concentration of copper in the catchment. From 3000  $^{14}\text{C}$  yrs BP, the number of fur seal hairs in the catchment does not decline below 1500 hairs, correlating with the increase in copper concentrations which increase from 2900  $^{14}\text{C}$  yrs BP, this being consistent with the 100 year lag as observed earlier in the record. Zinc behaves in a similar way, however, fluctuations below the threshold of 1500 hairs are observed.

Zinc and copper are possible indicators of fur seal activity however, this is dependant upon the size of the fur seal population as the fur seal hair abundance is relatively low and therefore, a significant fur seal population is required before the concentration of these elements is affected.

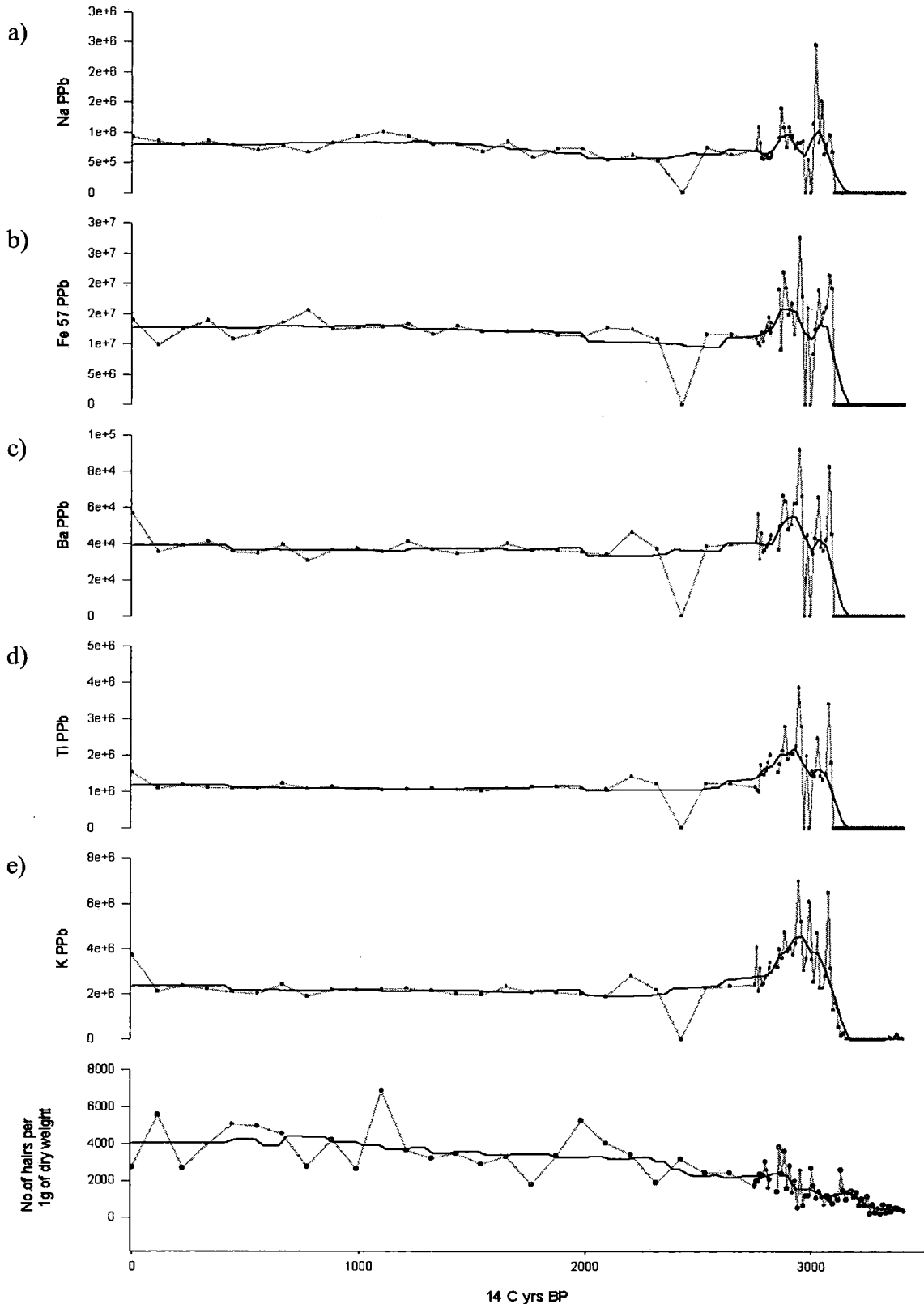


Figure 5.5: Element concentrations of group B compared to fur seal hair abundance, relative to age a) Potassium; b)Thallium; c) Barium; d) 57- Iron; e) Sodium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

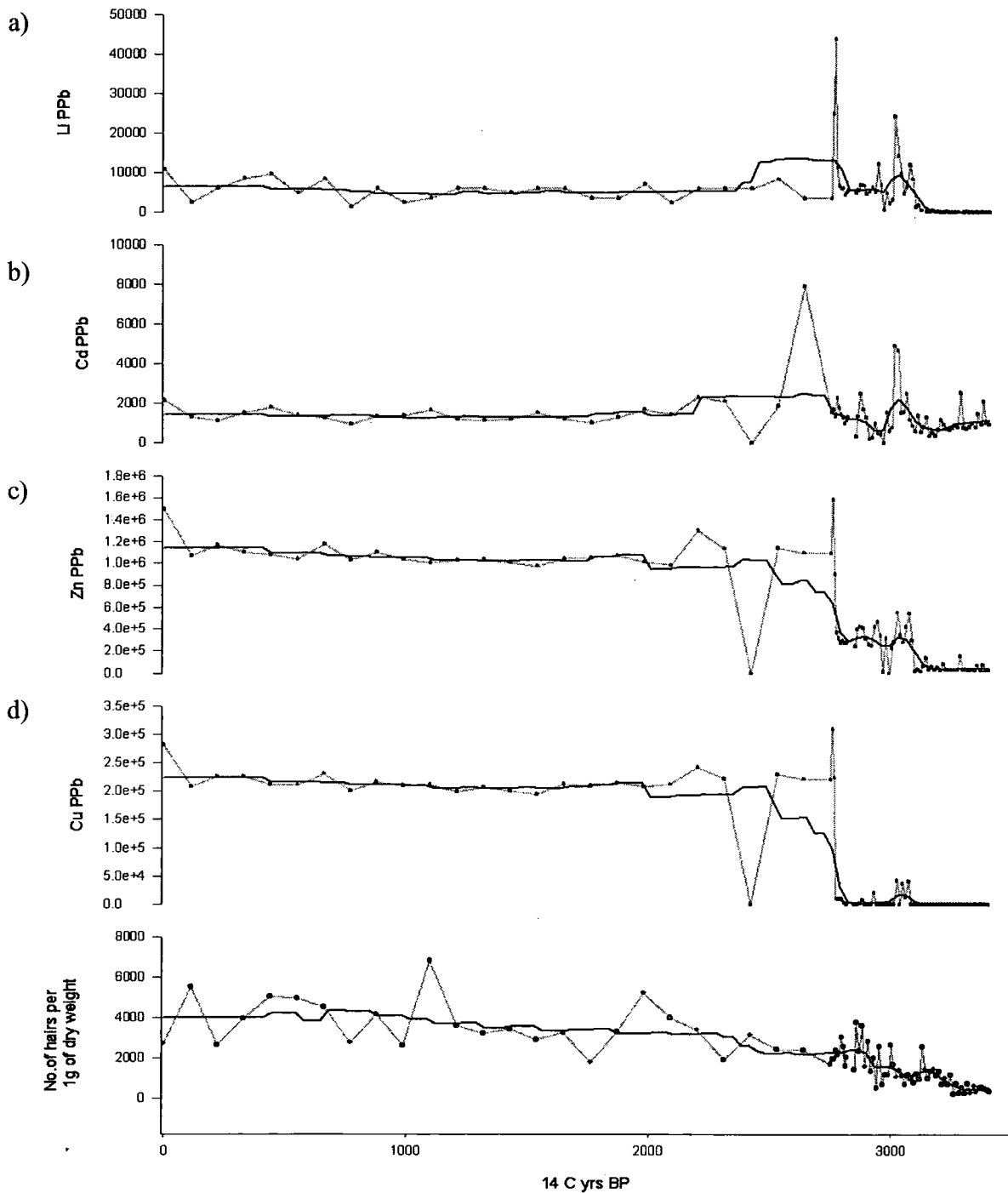


Figure 5.6: Element concentrations of group C compared to fur seal hair abundance, relative to age. a) Copper; b) Zinc; c) Cadmium; d) Lithium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 5.4.2.4 Group D (Bismuth, Molybdenum, Antimony, Thallium, Boron, Beryllium)

None of the elements in this group have previously been found to correlate with fur seal or penguin activity and as figure 5.7 shows, it does not appear that this record from Humic Lake shows a significant correlation. As the other elements in the group are considered non-essential to biology, it is not surprising that these element concentrations do not correlate with an increase in fur seals (Reimann and de Caritat 1998).

#### 5.4.2.5 Group E (Selenium, Vanadium, Calcium, Chromium, Manganese, Cobalt, 54-Iron)

The elements of group E are negatively correlated with fur seal hair abundance below 3000 hairs per 1g of dry weight. Above this threshold, these elements show no correlation with fur seal hair abundance, suggesting additional processes are operating in the catchment at this time, diluting the affect of fur seals on these element concentrations (see figure 5.8). The exception to this is vanadium and to some extent selenium, as the increase at 1100  $^{14}\text{C}$  yrs BP indicates that there are other factors influencing the concentrations of these elements in addition to fur seals. This will be considered later in this chapter (see section 5.6).

In previous studies, selenium and calcium have been found to correlate with biological activity, however, this does not appear to be the case in this catchment. This is likely to be the result of catchment characteristics dominating the fluctuations of these elements at South Georgia. Although it is possible that the size of the population in this study is not significant enough to influence the elements, in previous studies where seal hair abundance was a magnitude lower, selenium concentrations were closely correlated with fur seal hair abundance (Sun *et al.* 2004a). A disparity here is likely to be due to a more dominant force than fur seals influencing the selenium concentrations at South Georgia and hence, the fur seal signature is obscured.

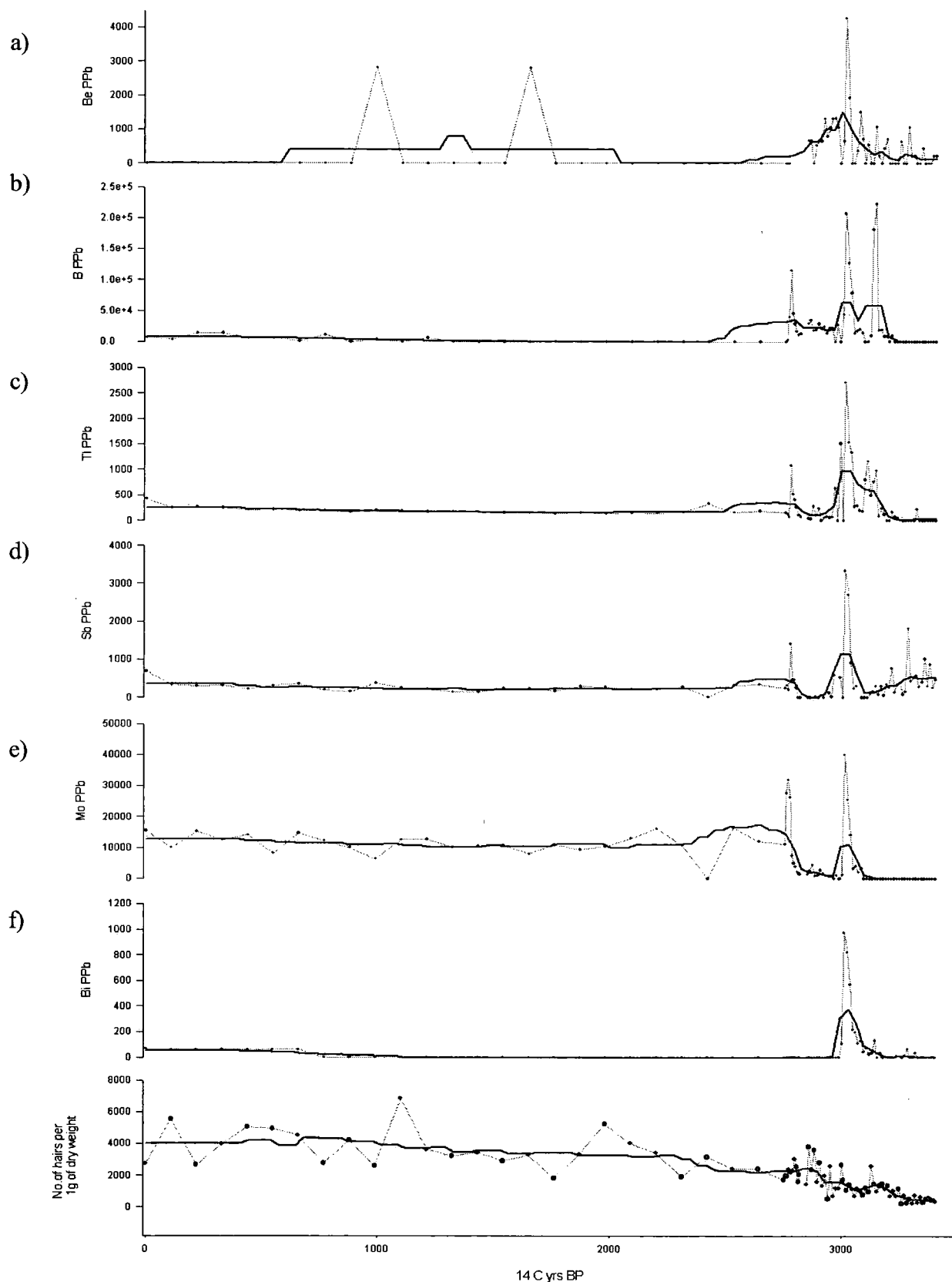


Figure 5.7: Element concentrations of group D compared to fur seal hair abundance. a) Bismuth; b) Molybdenum; c) Antimony; d) Thallium; e) Boron; f) Beryllium. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

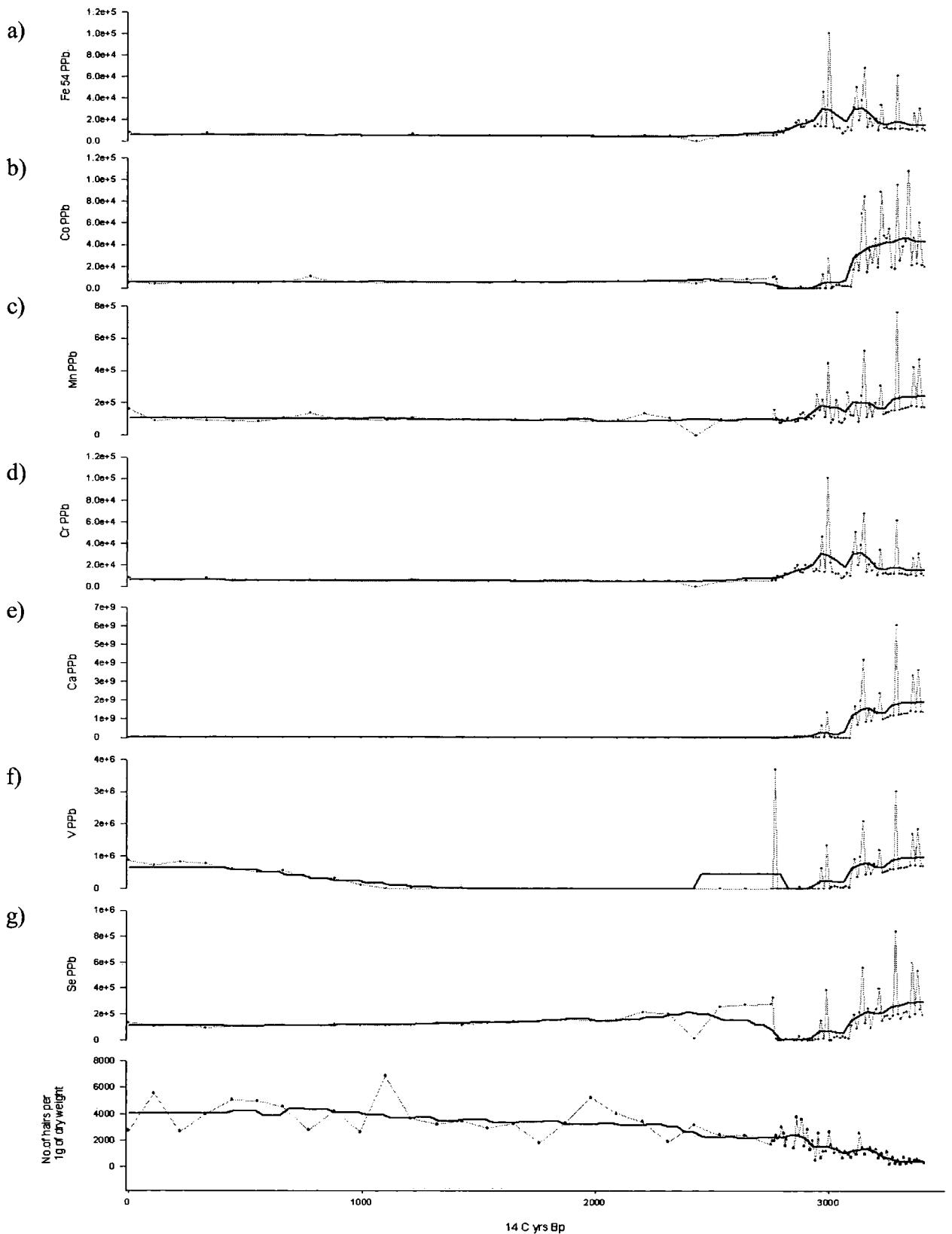


Figure 5.8: Element concentrations of group E compared to fur seal hair abundance, relative to age. a) Selenium; b) Vanadium; c) Calcium; d) Chromium; e) Manganese; f) Cobalt; g) 54-Iron. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

#### 5.4.2.6 Group F (Sulphur, Nickel, Arsenic)

As the elements in group F do not correlate significantly with each other, the elements are considered separately.

##### 5.4.2.6.1 Sulphur

Sun et al. (2004a) establish sulphur as a bio element for fur seals however, as figure 5.9a shows, there is very little correlation between the concentration of sulphur and fur seal hair abundance. It is possible that the sulphur concentrations at South Georgia do not correlate with fur seal hair abundance as concentrations do on King George Island due to the magnitude of eutrophication. As Holmer and Storkholm (2001) indicate, sulphur concentrations increase in eutrophic lakes. It is widely recognised that one of the impacts of fur seal population growth is the eutrophication of lakes, as fur seal populations increase, eutrophication in nearby lakes also increases. At Humic Lake, this does not appear to be the case, which is possibly a result of variable catchment characteristics and lake processes.

##### 5.4.2.6.2 Nickel

The nickel record is not complete therefore, any correlation with fur seal hair abundance is difficult (see figure 5.9b). Previously nickel has not been found to be a bio indicator and results suggest in this catchment, this is also the case, thus, it can be concluded that nickel cannot be used as a bio indicator for fur seals.

##### 5.4.2.6.3 Arsenic

The fluctuations in arsenic correlate significantly with fur seal hair abundance with the exception of a peak at the base of the core. From this evidence, As concentrations increase with fur seal hair abundance, with the exception of a peak at 3388  $^{14}\text{C}$  yrs BP. Previously arsenic has not been found as a bio marker as arsenic is not an element essential for biology therefore, in this case, it is unlikely that the fur seals are influencing the concentration of arsenic. The correlation is likely to be a result of a

change in the catchment to conditions more conducive to fur seal population growth and causing a change in the concentration in arsenic.

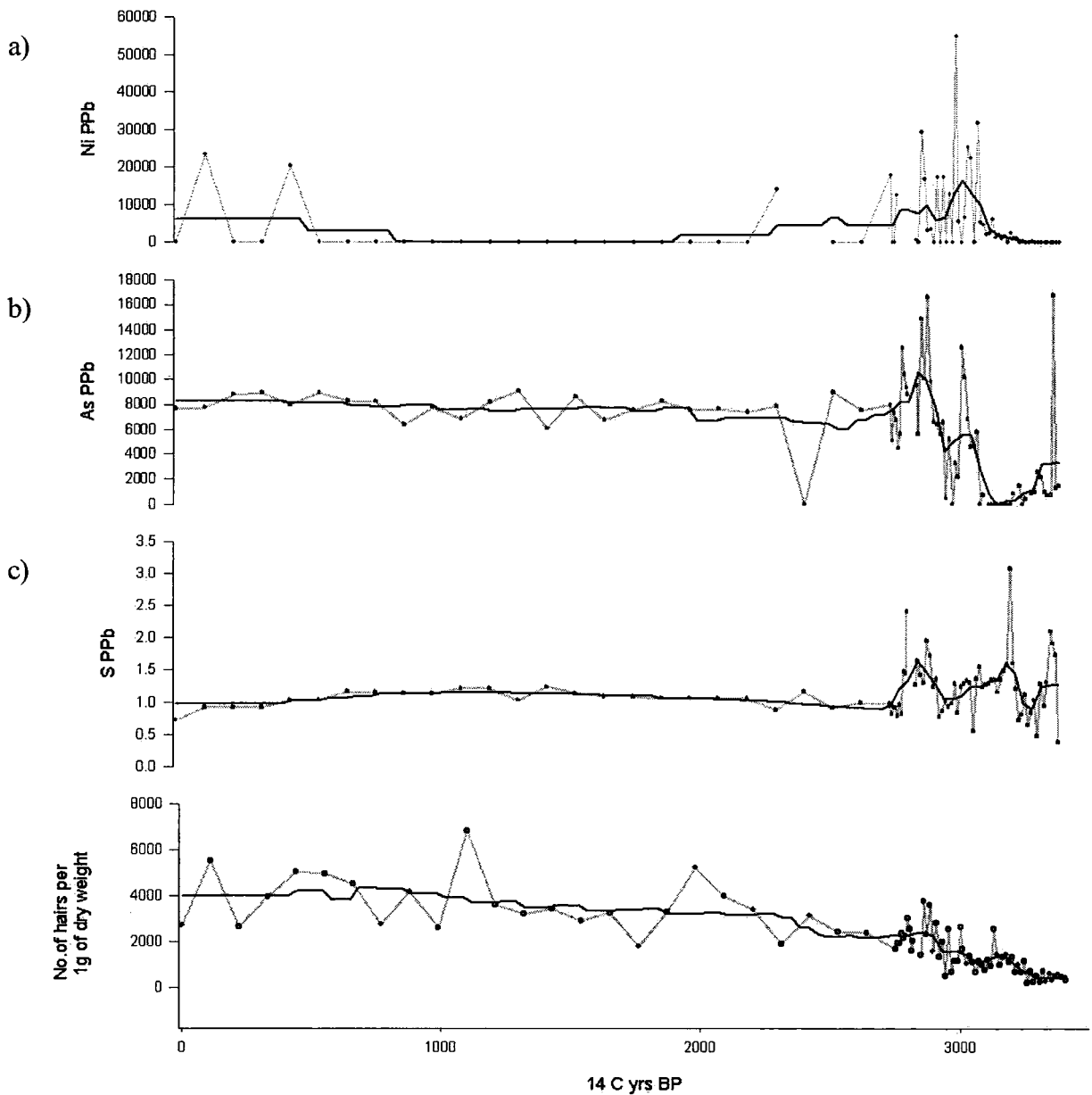


Figure 5.9: Element concentrations of group F compared to fur seal hair abundance relative to age. a) Sulphur; b) Arsenic; c) Nickel. The smooth line is the smoothed average calculated in Sigma Plot using the running average function, with sampling proportion set at 0.1.

### 5.4.3 Geochemical Summary

From the results of the geochemical analysis, *none* of the elements correlate significantly with the fur seal population changes and cannot be used solely as an indicator of fur seal population variation. This conflicts with evidence from Sun *et al.* (2004a) which highlighted selenium, sulphur, carbon (TOC), nitrogen (TN) and fluorine concentrations to fluctuate significantly with fur seal hair abundance (see figure 3.6). This difference can be related to the differing catchment conditions, such as catchment size, geology, vegetation cover and the differing magnitude of the fur seal population between the study sites. Although some elements correlate with the fur seal population at some points in the core, there appears to be additional factor(s) significantly influencing the element concentrations rather than fur seals. It is possible that the fur seal signature has been diluted at South Georgia due to more influential factors, for example a change in weathering regimes in the catchment or an alternative biological population (e.g. penguins). As the exact timing of these changes at the top of the core is unknown it is difficult to determine the possible effect these additional factors may have.

The elements most significantly correlated with fur seal hair abundance in this study are zinc and copper however, the concentration of these elements only increases once the fur seal population increases beyond 1500 hairs per 1g of dry weight. Below this level, the fur seal population may not be large enough to cause a considerable change in concentration. Although carbon and nitrogen correlate with fur seal abundance from 3439-2700  $^{14}\text{C}$  yrs BP, from 2700  $^{14}\text{C}$  yrs BP, carbon and nitrogen reach saturation in the catchment hence, very few of the fur seal hair abundance fluctuations after 2700  $^{14}\text{C}$  yrs BP are observed in the record. Comparing these findings with previous studies of fur seal geochemistry, it is clear that the influence of fur seals on the geochemistry of the catchment differs significantly between catchments and therefore, the elements from one study cannot be transferred to another. As a result of this it is difficult to use the geochemistry to validate the Hodgson *et al.* (1998) method of using fur seal hair abundance as a proxy for fur seal populations.

### 5.5 20<sup>th</sup> – 21<sup>st</sup> Century changes in fur seal populations

Although the fur seal population is known during the 20<sup>th</sup> century from census data, reconstructing the population in terms of fur seal hair abundance allows a comparison to be made between 20<sup>th</sup> century changes and the changes in the late Holocene.

Due to the unexpectedly low resolution of the fur seal hair abundance data at the top of the core, it is difficult to evaluate the recent changes in the fur seal hair abundance and hence, determine whether population growth in the 20<sup>th</sup> and 21<sup>st</sup> century is greater than any time in the past 3439 <sup>14</sup>C yrs BP (see figure 5.1). In this discussion I will assume the top sample (0 cm) is indicative of seal populations during the 20<sup>th</sup> century (see section 5.2.3). As figure 5.3 indicates, fur seal hair abundance has been increasing since at least 3439 <sup>14</sup>C yrs BP, therefore, it can be argued that this recent increase is part of a longer-term trend through the late Holocene. From figure 5.3 it is clear that a large increase in the fur seal hair abundance occurred at 1100 <sup>14</sup>C yrs BP to levels greater than the population at the top of the core, suggesting that South Georgia has the capacity to support a larger fur seal population than recent times. The increase from 3439 <sup>14</sup>C yrs BP to 2800 <sup>14</sup>C yrs BP is the largest increase in hair abundance in the past 3439 <sup>14</sup>C yrs BP and appears more significant than changes taking place towards the top of the core. This increase follows a very low fur seal hair abundance at 3439 <sup>14</sup>C yrs BP, from this it can be deduced that the greatest rate of increase in fur seals occurs when the population is near extinction. Using this theory, as the 20<sup>th</sup> century increase follows almost extinction of the fur seal population, it can be concluded that the rapid increase documented in the 20<sup>th</sup> and 21<sup>st</sup> centuries is part of the natural variability of the fur seal population, recovering from near extinction.

### 5.6 Environmental changes

As outlined in objective 4 (see section 1.3), this study has investigated the possible link between the fur seal population and the changes in climate on South Georgia as outlined in section 2.3. A second strand of the geochemical analysis was to evaluate the impact climate changes had on the geochemistry of the sediment. As summarised in section 5.4.3, geochemical fluctuations in the catchment do not correlate with the fur seal hair abundance. Although geochemistry cannot be used as a proxy for fur seal populations at Humic lake, fluctuations in the geochemistry may be occurring in response to environmental change. The rare elements deposited represents important

palaeoenvironmental signals (Engstrom and Wright 1978), therefore, the geochemical record can be used to provide further evidence for late Holocene environmental changes. This data and data outlined in section 2.3 (summarized in figure 2.11, 2.13) will be used as a basis on which to evaluate the impact of climate change on the fur seal population.

### 5.6.1 Geochemical signature

#### 5.6.1.1 Group A (Carbon, Nitrogen, Strontium, Aluminium)

As all the carbon in the sample is organic carbon, it can be inferred that this record provides an indication of past lake productivity (Last and Smol 2001). Assuming the dating model is correct, the plateau of carbon and nitrogen from 2700  $^{14}\text{C}$  yrs BP suggests that organic productivity in the catchment has not changed significantly from 2700  $^{14}\text{C}$  yrs BP to present. Previous studies of environmental change on South Georgia suggest a decrease in productivity, associated with climate deterioration at 2600  $^{14}\text{C}$  yrs BP (see figure 2.11). This disagreement in the record can be attributed the error in dating the sediments.

Strontium and Aluminium are not commonly used as indicators of environmental change and fluctuations in the catchment do not correlate with previous proxies used to reconstruct climate as shown in figure 2.11.

#### 5.6.1.2 Group B (Potassium, Titanium, Barium, 57-Iron, Sodium)

As Engstrom and Wright (1978) indicate, sodium and potassium concentrations increase in late glacial sediments in comparison to post glacial sediments. The high concentration of these elements from 3100- 2700  $^{14}\text{C}$  yrs BP, implies sediments are postglacial. This is in accordance with the climate shifts of South Georgia as this period was warm and dry. Associated with this warmer period, as figure 2.11 indicates, glaciers were retreating. Glacial retreat releases precipitation and inorganic sediment into the catchment hence, increasing the concentration of sodium and potassium in the catchment. Lowe and Walker (1998) also indicate sodium and potassium concentrations increase with soil erosion. Although this period is thought to be stable, as glaciers retreat, this releases precipitation in the catchment and hence, sediment transport

increases, further supporting the hypothesis that the period up to 2700  $^{14}\text{C}$  yrs BP was relatively warm.

At 2400  $^{14}\text{C}$  yrs BP, the concentration of sodium declines to 0ppb, suggesting an increased stability. This closely correlates with the cooling event at 2600  $^{14}\text{C}$  yrs BP, which may cause increased ice cover in the catchment hence, reducing and stabilising the inputs into the lake. From this point, potassium and sodium concentrations remain relatively constant, suggesting very few changes in the catchment stability from 2600  $^{14}\text{C}$  yrs BP. As figure 2.11 indicates, although glacial fluctuations occurred post 2600  $^{14}\text{C}$  yrs BP, the climate remained relatively cool and glacial fluctuations were not as great as 2600  $^{14}\text{C}$  yrs BP. The concentration of sodium and potassium is likely to have been maintained from a constant supply of glacial till from within the catchment.

#### 5.6.1.3 Group C (Copper, Zinc, Cadmium, Lithium)

As stated in section 5.4.2.3, copper and zinc correlate with the fur seal population fluctuations hence, these elements cannot be used as indicators of climate change. Cadmium and lithium however, do not correlate with fur seal hair abundance and it is possible that fluctuations in these elements reflect a climate signature. The coupling of cadmium, lithium, copper and zinc prior to 2700  $^{14}\text{C}$  yrs BP suggests the climate was relatively stable and the fur seal population was not significant enough to alter these element concentrations. At 2700  $^{14}\text{C}$  yrs BP a significant change in the catchment occurred, correlating with other element groups to suggest deterioration in climate. The lithium and cadmium concentrations decline rapidly following this increase to suggest a brief change as conditions returned to similar levels prior to this increase. Although the climate records (see figure 2.11) suggest this is not the case, it is possible that following the change at 2700  $^{14}\text{C}$  yrs BP, the change in catchment conditions resulted in other element concentrations to increase and hence, the relative concentration of lithium and cadmium in the catchment declined. Previous studies suggest that cadmium and lithium are not used extensively as indicators of climate change and hence, very little of the climate signature can be deduced from this record.

#### 5.6.1.4 Group D (Bismuth, Molybdenum, Antimony, Thallium, Boron, Beryllium)

Although these elements are not commonly used as indicators of environmental change, they may be used to provide an indication of catchment change. Element concentrations peak slightly at 3000  $^{14}\text{C}$  yrs BP, although this is not significant in all records, the peak in boron is the largest in the whole record. The climate at this point (see figure 2.11) does not appear to change dramatically, remaining warm and stable. Concentrations remain relatively low following this peak, with the exception of a peak at 2773  $^{14}\text{C}$  yrs BP, however, this does not significantly correlate with other element groups. All the peaks in concentrations occur pre 2773  $^{14}\text{C}$  yrs BP, prior to the dramatic climate cooling (see figure 2.11) hence, suggesting that these elements are abundant during warm phases, as concentrations are very low or at 0ppb after this time. It is possible that these fluctuations are showing changes in the warm period, which is not widely documented in the literature. However, very few of these elements are commonly used as environmental indicators therefore, this cannot be substantiated without further analysis. It can be concluded that the elements in group D do not clearly reflect fur seal population changes or climate changes during the past 2700  $^{14}\text{C}$  yrs BP.

#### 5.6.1.5 Group E (Selenium, Vanadium, Calcium, Chromium, Manganese, Cobalt, 54-Iron)

As Matsumoto (1993) indicates, cobalt, iron, manganese, copper and nickel are a major source of chemical weathering. Although copper and nickel are not correlated in this group, as I outlined in section 5.4.2.3, copper is influenced by fur seal activity therefore, chemical weathering does not solely influence concentrations. The nickel record is incomplete, making correlation difficult. From cobalt, iron, manganese record and the hypothesis that these elements are a major source of chemical weathering, it can be deduced that chemical weathering was greatest at 3439  $^{14}\text{C}$  yrs BP, declining to a minimum at 2750  $^{14}\text{C}$  yrs BP. From this point levels remain relatively constant with the exception of a dramatic decline at 2400  $^{14}\text{C}$  yrs BP.

This compares with the climate changes inferred from other studies (see figure 2.11). At the base of the core although the climate is warm and stable glaciers are retreating, suggesting an increase in sediment input into the catchment. These sediments are likely to be glacial origin and primarily minerogenic matter. The concentration of these

elements decline to a minimum at 2750  $^{14}\text{C}$  yrs BP. This decline can be correlated to glacial expansion documented in other proxy records (see figure 2.11) occurring at approximately 2600  $^{14}\text{C}$  yrs BP hence, restricting the inputs into the lake and the catchment. Although the catchment has not remained glaciated for the period since 2750  $^{14}\text{C}$  yrs BP, the climate has remained relatively cool and there has not been a significant glacial retreat to release a large amount of sediment into the catchment.

### 5.6.2 Climate change inferred from geochemistry

Due to the resolution of the record and the dating error, it is difficult to identify climate small climate changes within the sediment record. From the sediment record, 6 distinct climate changes can be identified which can be correlated to the climate record (shown in italics) as observed in figure 2.11 and 2.13.

- 3400-3100  $^{14}\text{C}$  yrs BP (*Pre 2600  $^{14}\text{C}$  yrs BP*)

Element concentrations are minimal, suggesting very few inputs into the lake during this period. This correlates with the late Holocene Climate Optimum as documented in the literature to suggest a warm, dry and stable period (Rosqvist and Schuber 2003). Although glaciers are retreating, glacial extents are more restrained than today and therefore, not affecting the catchment at Maiviken (Clapperton *et al.* 1989).

- 3100-2700  $^{14}\text{C}$  yrs BP

Concentrations in elements increase, signifying an increase in weathering and sediment flux into the lake, similar to conditions documented from palaeolimnological studies in other lakes in the Maiviken area (see figure 2.13) (Birmie 1990; Clapperton *et al.* 1989). This increase in instability can be correlated to climate deterioration, causing an increase in weathering and instability in the catchment. This releases a large amount of sediment into the catchment, causing element concentrations to increase.

- 2700-2300  $^{14}\text{C}$  yrs BP (*Climate deterioration 2600  $^{14}\text{C}$  yrs BP*)

Element concentrations plateau as the catchment stabilises following a climatic cooling and associated increase in annual ice cover in the catchment (see figure 2.11). Although

the entire catchment is not glaciated, the cooler climate increases the ice cover on the lake and small cirque glaciers within the catchment expand, reducing the sediment availability in the catchment. The radiocarbon date obtained at 183cm point suggests the sedimentation rate had decreased from 3400  $^{14}\text{C}$  BP by 2750  $^{14}\text{C}$  yrs BP.

- 2310-1320  $^{14}\text{C}$  yrs BP

The slight increase in element concentrations at this stage and correlation with other proxy climate records suggests that climate begins to ameliorate, however remains relatively stable. Clapperton *et al.* (1989) suggests that glaciers are advanced, therefore, restricting the sediment input into the catchment.

- 1320-770  $^{14}\text{C}$  yrs BP (*Cooling 1000  $^{14}\text{C}$  yrs BP*)

Element concentrations in group B increase at 1320  $^{14}\text{C}$  yrs BP, suggesting an increase in weathering and sediment input into the catchment. This can be correlated to the cool climate as documented by Rosqvist and Schuber (2003) which caused glacier fluctuations and an increase in instability in the catchment. This instability releases sediment (primarily glacial till) into the catchment, however this release is not as notable as the change at 2700  $^{14}\text{C}$  yrs BP.

- 770  $^{14}\text{C}$  yrs BP- Present

Element concentrations are stable at this point in the core, suggesting that the climate has remained stable and relatively cool from 770  $^{14}\text{C}$  yrs BP to present. Although Clapperton *et al.* (1989) and Hayward (1983) document glacial fluctuations in the past 200 years, these fluctuations have not affected the lake catchment in this study due to its low attitude and small catchment size.

#### 5.6.2.1 Summary

From the results of the geochemistry and other proxy records, figure 5.10 summarises the climate changes in the catchment.

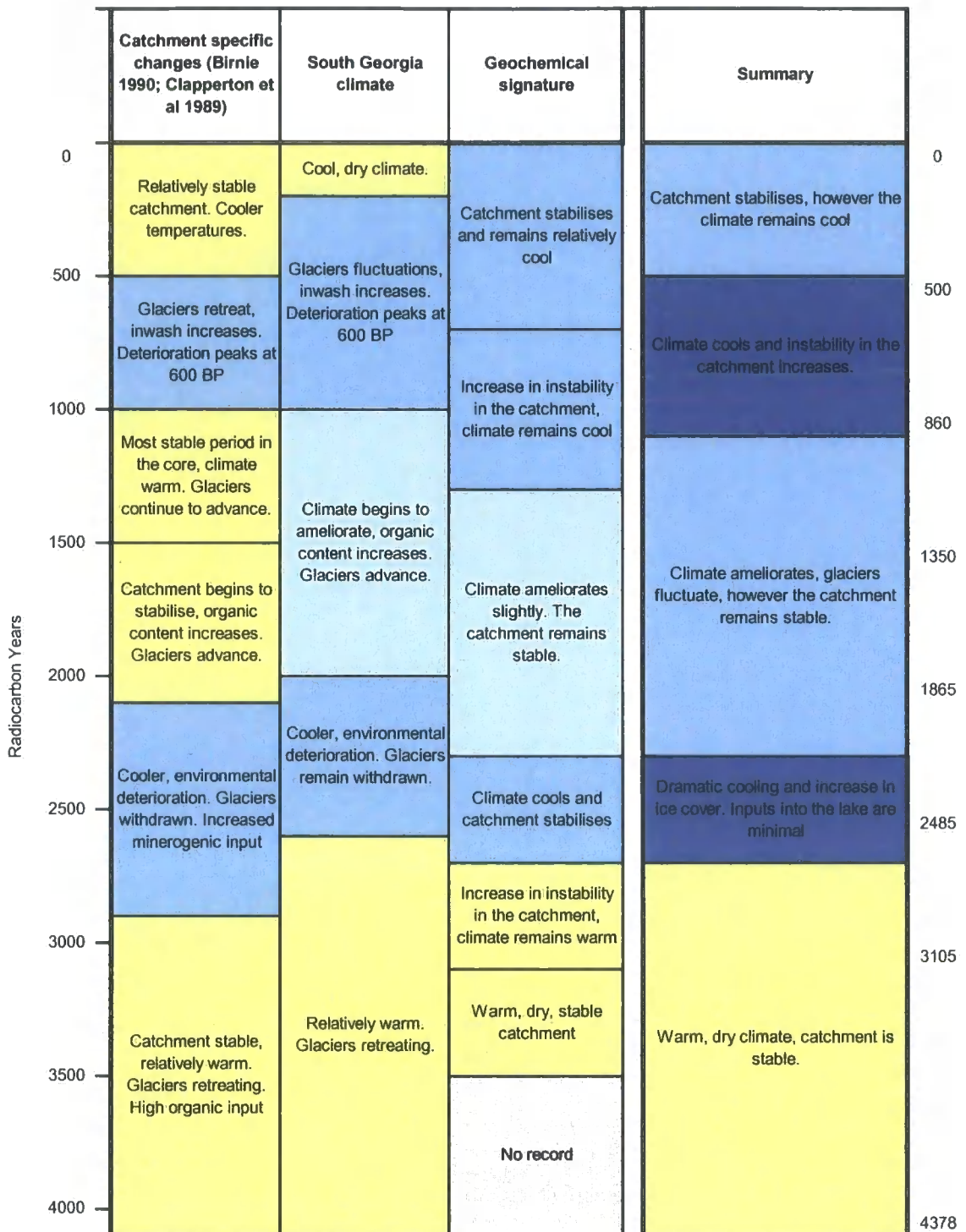


Figure 5.10 – Summary of the climate changes occurring within the catchment from proxy records and geochemical analysis from Humic Lake.

## 5.7 Fur seal population fluctuations relative to climate change.

The climate changes as outlined in figure 5.10 are correlated with the fur seal hair abundance record to evaluate the effect of climate change on the fur seal population.

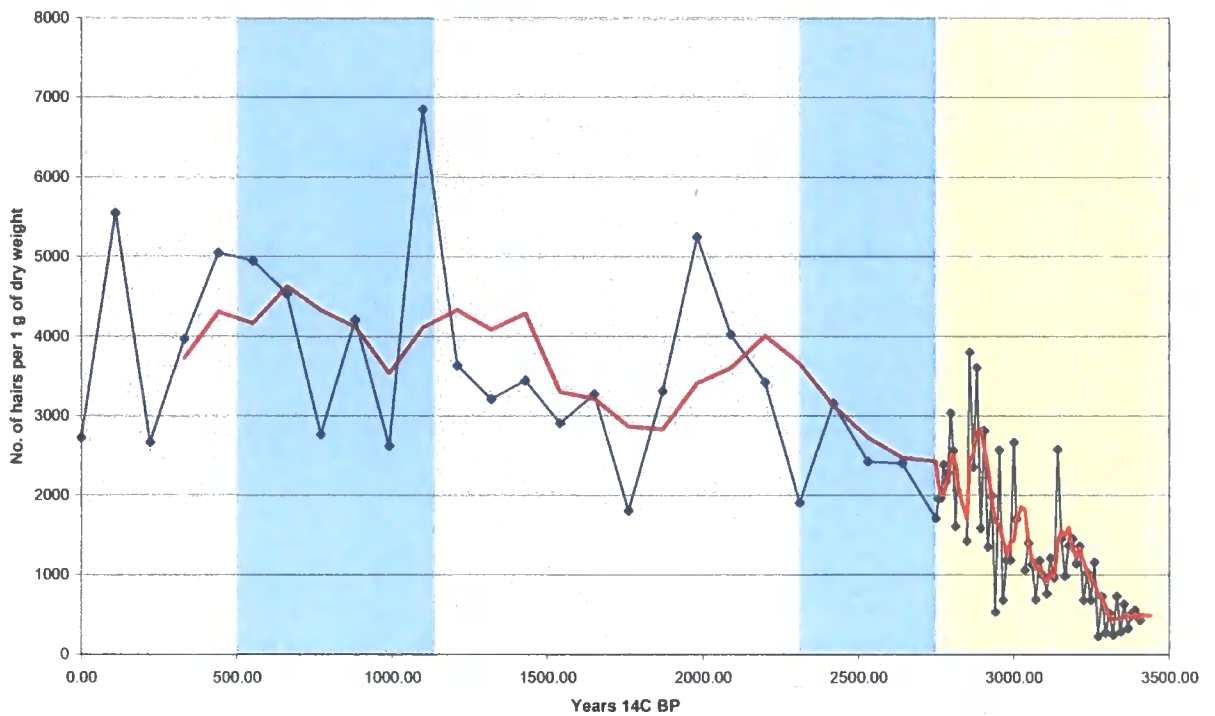


Figure 5.11a: Fur seal hair abundance fluctuations and climate changes at South Georgia. The yellow section represents a warm period, blue sections represent a cooling and darker blue marks an enhanced cooling.

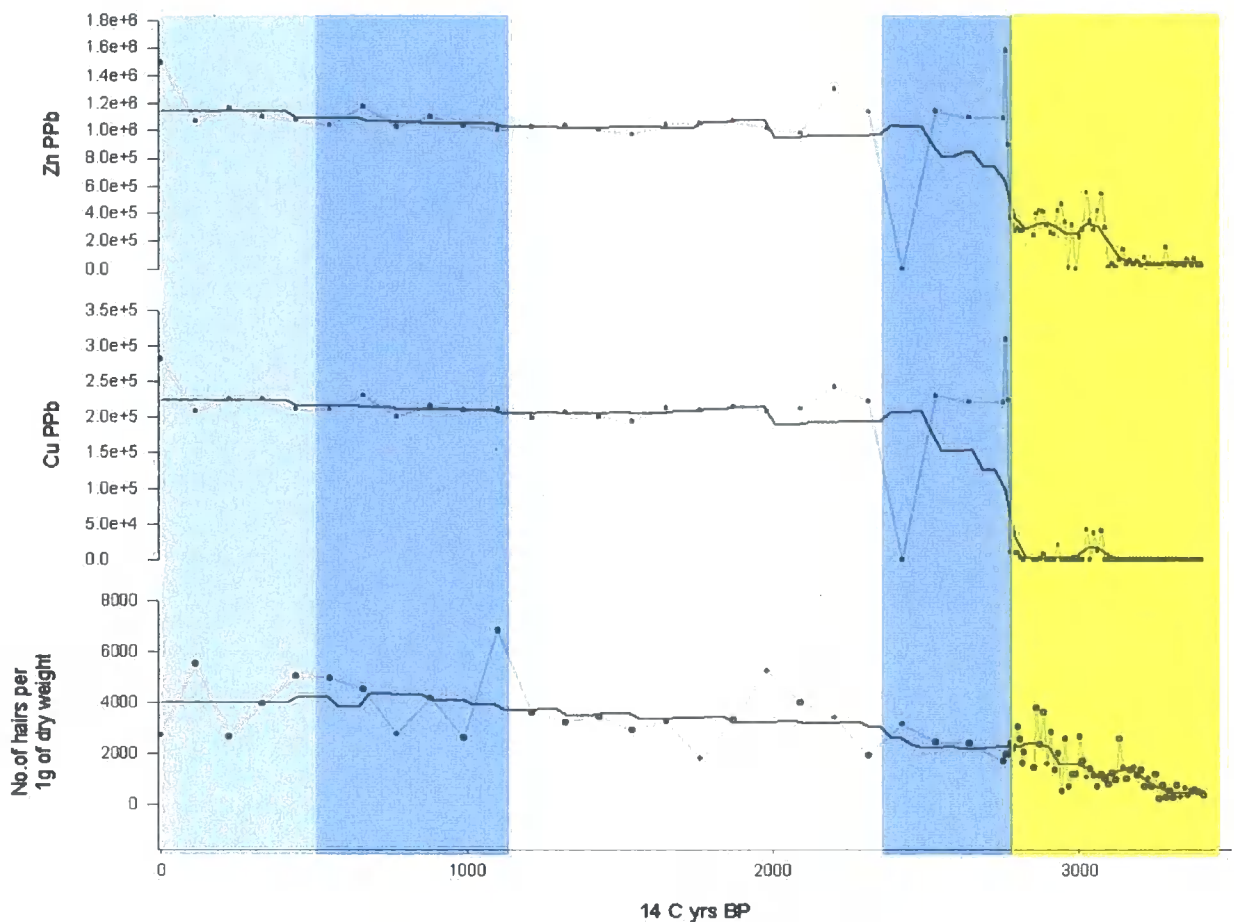


Figure 5.11b: Fur seal hair abundance fluctuations correlated with copper and zinc fluctuations and climate changes at South Georgia.

### 5.7.1 Late Holocene Climate Optimum (Pre 2600 $^{14}\text{C}$ yrs BP)

The low concentration and minimal fluctuations of elements in group A, B, C and D suggest that the catchment was warm and stable from 3400-3100  $^{14}\text{C}$  BP. This is in agreement with other records from South Georgia that suggest a warm dry period (see figure 2.11 and 5.10). As figure 5.11 indicates, at this time, the fur seal population was at a minimum for the past 3439  $^{14}\text{C}$  yrs BP, suggesting that warmer conditions are not favourable for fur seal population growth.

The most significant change in the geochemical record occurred at 3100  $^{14}\text{C}$  yrs BP, as weathering and instability increased in the catchment, increasing the inputs into the lake and hence, the rapid increase in element concentrations. This change at 3100  $^{14}\text{C}$  yrs BP correlates with a plateau in the fur seal record, suggesting that although the population were not negatively affected by climate change, it caused a stagnation of the population, before then increasing again at 2900  $^{14}\text{C}$  yrs BP.

### 5.7.2 Climate Deterioration (2600-1600 $^{14}\text{C}$ yrs BP)

It is widely documented that the warmer period ceased at 2600  $^{14}\text{C}$  yrs BP, when a significant cooling occurred (see figure 5.10). During the cooler period, an increase in ice cover reduced the inputs into the lake causing a decline in the element concentrations.

The fur seal record peaks slightly at this point, as part of a longer-term trend of increase, suggesting that this brief glacial period was favourable for fur seal population growth, however, did not dramatically affect the fur seal population.

A larger increase in the fur seal population is observed at 1980  $^{14}\text{C}$  yrs BP, yet at this point in the geochemical record there are no significant changes in any of the element concentrations. In the climate record however, there does not appear to be a significant climate change at this point. As figure 2.11 indicates, most climate records indicate this was a period of cooling, sustained from the widely documented climate deterioration at 2600  $^{14}\text{C}$  yrs BP.

### 5.7.3 1100- 200 $^{14}\text{C}$ yrs BP

The largest peak in the fur seal population in the past 3439  $^{14}\text{C}$  years occurred at 1100  $^{14}\text{C}$  yrs BP. Although this peak was brief, it is significant as the fur seal hair abundance increases by a factor of 2 at this point. The geochemical record and other proxy records suggest that the climate cooled and instability in the catchment increased from 1100  $^{14}\text{C}$  yrs BP and was sustained until 500  $^{14}\text{C}$  yrs BP.

Although the fur seal population increase was not sustained during this cooling period (see figure 5.11), as I stated in section 5.4, the fur seal population cannot be sustained above 4000 hairs per 1 g of dry weight at Humic Lake, therefore, although external

factors such as climate allow the population to increase, internal factors such as competition for breeding ground between seals appears to limit the population.

The fur seal hair abundance remains relatively constant from 660  $^{14}\text{C}$  yrs BP, with the general increase ceasing. There is however a notable peak at 440  $^{14}\text{C}$  yrs BP. Due to the change in sedimentation rate, and low resolution it is possible that this peak is in response to the cooling at 600  $^{14}\text{C}$  yrs BP described by Birnie (1990).

#### 5.7.4 200 $^{14}\text{C}$ yrs BP- present

The most recent climate record is derived primarily from historical records, rather than proxy data. As the resolution of the core at this point is not known exactly (as outlined in section 5.2.3), the core record cannot be used to accurately infer the fur seal hair abundance and climate changes.

As highlighted in section 2.5 the fur seal population during the past 200  $^{14}\text{C}$  yrs BP declined significantly and consequently increased dramatically from 1930 AD. Relating this to climate changes (see figure 2.16) fur seal population increases broadly correlate with climate warming.

#### 5.7.5 Summary

Figure 5.11 shows a summary of the fur seal abundance record in relation to the climate changes through the late Holocene. From 3439  $^{14}\text{C}$  yrs BP, when the record began to 2700  $^{14}\text{C}$  yrs BP the climate was warm, possibly warmer than today in a period known as the late Holocene optimum. Through this period the fur seal hair abundance in the core gradually increases.

Although the geochemical record suggests climate deterioration commenced earlier than the climate record, the peak of cooling occurred from 2700 - 2400  $^{14}\text{C}$  yrs BP (see figure 5.10). The climate remained cool post 2400  $^{14}\text{C}$  yrs BP however, at this point, there is not a significant change in the fur seal hair abundance. As figure 5.10 suggests, this was a period of increased ice cover hence, inputs into the lake at this time were minimal restricting inputs into the lake. The peak in fur seal hair abundance at 2000  $^{14}\text{C}$  yrs BP, suggests cooler conditions are favourable for fur seal population growth.

As figure 5.11 shows, the climate cooled from 1100  $^{14}\text{C}$  yrs BP (Birnie 1990), again correlating with an increase in the fur seal hair abundance however, this increase is not sustained through the cooling period as the population rapidly declines back to previous levels and continues to gradually increase to the top of the core.

### 5.8 Factors controlling fur seal population changes in the late Holocene

During the late Holocene, although fur seal populations have continually increased from 3439  $^{14}\text{C}$  yrs BP, perhaps reflecting the recovery of the population following the Holocene Climatic Optimum, larger peaks in the population generally correlate with colder periods (see figure 5.11). Although the core does not extend back to the Holocene Climatic Optimum, at 3439  $^{14}\text{C}$  yrs BP, the population was very low suggesting that the climate conditions were not conducive to fur seal population growth. As the climate cooled, fur seal population growth increases dramatically.

As discussed in chapter 2, the prime factors influencing fur seal population growth are prey availability and predator competition therefore, it can be inferred that at South Georgia, as the climate cools, prey availability and predator competition become more favourable for fur seal population growth.

#### 5.8.1 Prey availability

Assuming krill has been the primary prey for the fur seal through the late Holocene, it appears that krill availability is more favourable for fur seals during cooler climates. Although there is no single environmental variable found to show a reliable and predictable relationship for distribution of krill relative to climate, broad scale relationships have been found relating to temperature and oceanic fronts (Trathan *et al.* 2002).

The krill population at South Georgia is not self-sustaining, with the majority of krill transported to the region from the Antarctic Peninsula, South Orkney and the Weddell Sea via the ACC (Antarctic Circumpolar Current) (Reid *et al.* 1999; Meredith *et al.* 2005; Hofmann and Murphy 2004). Variability in the krill population is thought to be a consequence of the amount of krill that becomes entrained within the ACC at sites upstream of South Georgia or as a result of the spatial and temporal variability in the transport mechanism itself (Hofmann and Murphy 2004). The magnitude of this change

is dependant upon how much the front moves, how quickly it returns to its former position and the time of year the movement occurs (Trathan *et al.* 2003). As the atmosphere and ocean are a highly coupled system, changes in oceanography are simultaneous with changes in terrestrial temperature hence, correlating with climate changes. The precise movement of these oceanographic fronts through the late Holocene is debatable and therefore, the exact movement of these fronts cannot be accurately correlated with fur seal population changes to determine whether this influenced the growth of the fur seal population. At present, areas of high krill abundance are located in the area between the SACCF and the SACCB, close to the sea ice boundary (see figure 5.12). The location of these fronts is highly variable. During colder, glacial periods, the polar frontal zone is located further north and therefore, increases the proximity of the SACCF in relation to South Georgia hence, the krill transported into the ocean waters surrounding South Georgia reduces (Thorpe *et al.* 2002). During warmer periods, the SACCF is located further south of South Georgia, again reducing the krill transported to South Georgia. Optimum conditions for krill transport are debatable, however, are thought to occur in a climate between these warm and cold extremes.

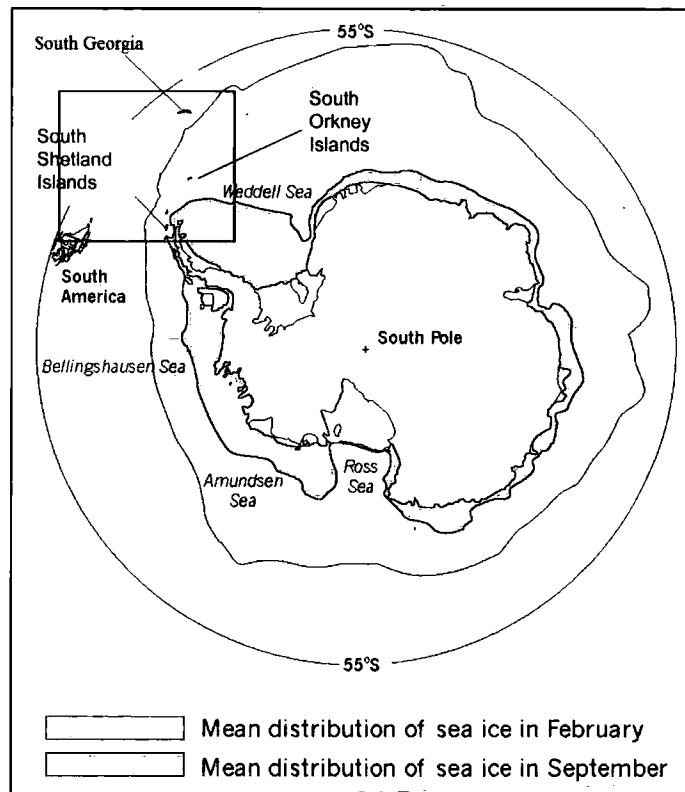


Figure 5.12b: Mean-sea ice boundary relative to South Georgia, South Shetland and South Orkney Islands. The section in the red box is enlarged in figure 5.12b. Adapted from Hansom and Gordon (1998).

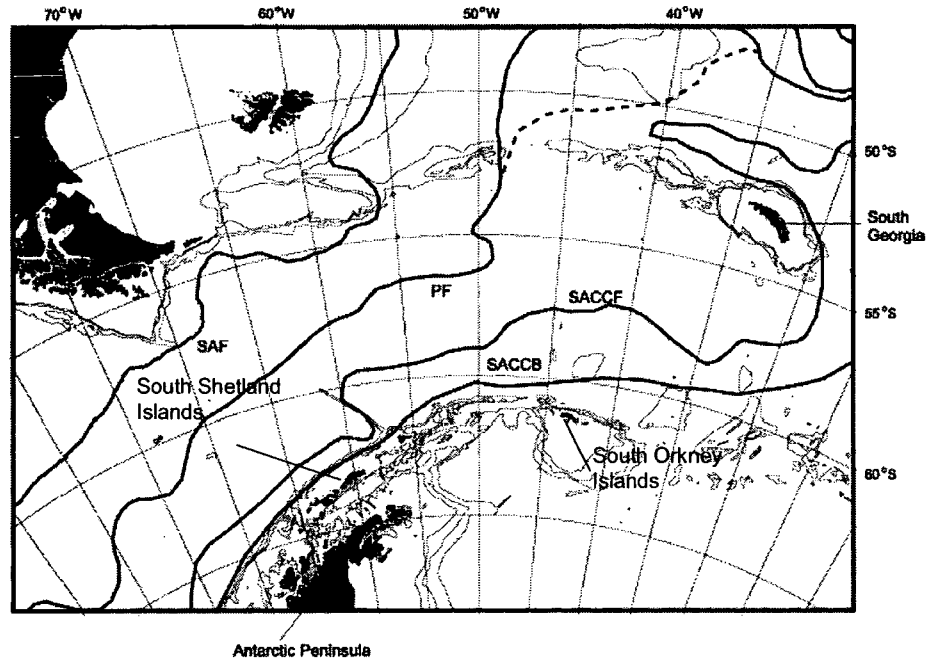


Figure 5.12b: Scotia Sea region showing South Georgia relative to key oceanographic features which influence the distribution of krill. Sub-Antarctic front (SAF), Polar Front (PF) (dashed line indicates the position of the Polar Frontal Zone), and the Southern Antarctic Circumpolar Current Front and Boundary (SACCF; SACCB). (Source: Murphy and Reid 2001)

As Murphy and Reid (2001) indicate, today krill at South Georgia are on the northern edge of their distribution and stock relies on immigration associated with regional current systems. As the climate changes, the krill track shifting climate and hence, the distribution of krill alters in relation to climate change (Walther *et al.* 2002). During periods relatively cooler than today krill were more abundant and thus, the prey availability for fur seals increased. Alternatively, during warmer periods, the northern extent of krill was located further south than today, thereby decreasing the prey availability for fur seal populations at South Georgia.

Despite this, it must be noted that, krill populations declined in 1998/99 and 2000/01, both of these years being linked to cold anomalies in the Southern Ocean. In 2000/03 these changes are thought to be the result of changes in the path of the SACCF bringing colder water closer to South Georgia than in other years (Meredith *et al.* 2005). The cold anomaly in 1998/99 is linked to the 1997/98 El Niño event and is not directly linked to the changes in the path of SACCF and hence, the krill distribution at South

Georgia. Although it is widely recognised that El Nino events do affect krill distribution, the affect of this at South Georgia has not been fully quantified and will not be considered in detail here. These different factors affecting krill distribution illustrates how complex the system is and krill distribution cannot be solely defined as dependant upon the SACCF. Although this has implications for analysis and must be considered, these cold anomalies were annual events and therefore, the changes experienced during a cooling of the magnitude at 2600  $^{14}\text{C}$  yrs BP is likely to be greater than this annual variability.

Alternative evidence suggests that patterns in sea ice distribution and abundance affect krill productivity and recruitment (Reid *et al.* 1999; Murphy *et al.* 1998). A reduced krill biomass is thought to be associated with periods of low ice extent. From this it can be inferred that in a colder period, ice extent is greater and hence, is more favourable to greater regional immigration of krill into the South Georgia area. In warmer periods, sea ice declines and krill abundance falls hence, agreeing with the correlation found in figure 5.11.

Smith *et al.* (1999) outline a model for adélie penguin growth in relation to sea ice distribution. Here population growth increases during conditions of moderate sea ice cover, between extremes of excessive and insufficient ice cover. Although fur seal populations at South Georgia grow during colder periods, an extreme cold situation does not appear to have been reached during the late Holocene as the population does not show any indication of decline during cold periods. However, this is only a hypothesis and it is not clear how oceanography and sea ice variability are linked and how this may affect krill distribution. Conversely, evidence presented by Hofmann and Murphy (2004) suggests that the distribution of krill does not show any relationship with winter sea ice distribution or fronts.

### 5.8.2 Predator competition

Although prey availability is a fundamental factor affecting fur seal population growth, predator competition also plays an important role (see section 2.7.3.2). Sea ice extent increases in response to oceanographic and climatic changes. Changes in sea ice as Boveng *et al.* (1998) highlight, increase the abundance of leopard seals, a fur seal predator. During cooler periods, although prey availability increases, it is also possible

that the predator competition increases. As Boveng *et al.* (1998) argue, the predator competition on the South Shetland Islands is greater than at South Georgia due to the location of South Shetland Islands relative to the position of sea ice (see figure 5.12). The point of optimum fur seal population growth is likely to occur when sea ice increases and hence, increases the abundance of krill but not to such an extent to increase leopard seals, thus, fur seals perhaps survive when sea ice extent is not at its maximum extent but to a greater extent than today. This would explain why the fur seal population did not notably increase during the coldest periods, as the sea ice may have been too extensive, thereby increasing the predator competition. As the climate warmed slightly from the maximum cold period, sea ice declined thus, decreasing the predator competition whilst krill availability was still enhanced sufficiently to allow population growth.

Increased sea ice extent is also likely to bring other changes such as a variation in species, and perhaps increasing the competition for krill. For example, as I stated in section 2.7.3.1.1, emperor penguins are positively correlated with sea ice extent and therefore, the increase in these species may affect the availability of krill due to the increased competition. Alternatively, increased sea ice extent is likely to cause a decline in some species (e.g. adélie penguins), therefore, reducing the competition for prey. Although these factors must be considered, this change in species is unlikely to have greatly affected the fur seal population due to the dynamic nature of ecosystems, as although some species may be unable to survive, different species are likely to increase with the change in conditions.

### 5.8.3 Summary

Fur seal populations at South Georgia appear to increase during cooler periods. However, due to the complex interactions between the ocean and atmosphere, it is difficult to ascertain the reasons for this increase in fur seal populations during cold periods. Evidence from past studies suggests that the primary influence on fur seal population growth is prey availability (krill) (see section 2.7.4). This increase in prey availability is either a consequence of ocean currents moving northward or an increase in sea ice or possibly (due to the highly coupled oceanographic system) a combination of both factors. A change in oceanography alters the sea ice extent, which increases the availability of krill and therefore, increases the prey availability for fur seals. During

warmer periods, sea ice extent decreases and the availability of krill declines. Although to fully understand the reasons for the increase in fur seal populations, krill dynamics in relation to oceanographic changes must be understood further. As I have outlined in section 5.8.2, predator competition is a potential influential factor on the fur seal population growth, however, the knowledge of predator competition on South Georgia is limited. To accurately correlate fluctuations in predator competition with fur seal population changes, the interactions of the predators at South Georgia must be understood.

### 5.9 Recent changes

Although it is difficult to determine changes in recent fur seal populations through the 20<sup>th</sup> century from this study, it can be stated that fur seal populations have increased dramatically through the late Holocene and therefore, increases noted today are not unprecedented. Although the magnitude of change is unprecedented, the trigger for this change does not correlate with the factors affecting population growth during the late Holocene. As discussed in section 5.8, prior to human intervention fur seal populations increased during cooler periods as a consequence of abundance in krill. This increase in krill is closely correlated to an increase in sea ice extent. As the climate during the 20<sup>th</sup> century is warming, it is expected that the fur seal population would decline. However, it is widely recognised that the population has increased (see figure 2.17) due to a rise in prey availability caused by the sealing and whaling industries in the 19<sup>th</sup> Century (see section 2.7.2). As these activities are human induced, it can be concluded that fur seal population changes in the 20<sup>th</sup> century are a result of human induced change, creating a population growth of fur seals to a greater magnitude than natural environmental changes during the Holocene.

### 5.10 Past studies

Comparing these results to the study by Sun *et al.* (2004a) and Hodgson *et al.* (1998), this conclusion does not appear to be valid at Signy Island or King George Island.

#### 5.10.1 Hodgson *et al.*'s. (1998) study – Signy Island.

Evaluating the fur seal population reconstruction at Signy Island with South Georgia, there does not appear to be any significant correlation (see figure 3.2). The fur seal

population at Signy Island does not show any significant peaks through the past 6570  $^{14}\text{C}$  yrs BP, with the exception of a rapid increase from the 1970's to the present day. Fur seal hair abundance is also a magnitude lower here than the records at South Georgia.

#### 5.10.2 Sun *et al.*'s. (2004a) study – King George Island

Sun *et al.* (2004a) reconstruct the fur seal population on King George Island for the past 2367  $^{14}\text{C}$  yrs BP. The record of the fur seal population (see figure 3.6) suggests that the population increased from 1400-1100  $^{14}\text{C}$  yrs BP and 750-500  $^{14}\text{C}$  yrs BP, hence, presenting a similar picture to that of the South Georgia record (see figure 5.2).

The first peak from 1400-1100  $^{14}\text{C}$  yrs BP correlates with a peak at 1100  $^{14}\text{C}$  yrs BP in the record from South Georgia (see figure 5.2). The increase at South Georgia commences at approximately 1320  $^{14}\text{C}$  yrs BP however, due to the low resolution this is difficult to evaluate exactly. This peak in the South Georgia record suggests that the fur seal population increase lags the King George Island population increase by approximately 100 years. The second peak in the record by Sun *et al.* (2004a), from 750-500  $^{14}\text{C}$  yrs BP correlates with the peak at 440  $^{14}\text{C}$  yrs BP at South Georgia. Further suggesting population increase lags the King George Island population by approximately 100 years. Although the record at King George Island extends back to 2300  $^{14}\text{C}$  yrs BP, the evidence suggests that the fur seal population has been present on the island from only 1400  $^{14}\text{C}$  yrs BP (see figure 3.6), significantly shorter than the population at South Georgia.

The strong correlation between the record at King George Island and South Georgia suggests that a regional forcing factor such as a climate change was causing a fur seal population increase at approximately 1100  $^{14}\text{C}$  yrs BP and 500  $^{14}\text{C}$  yrs BP. Although fluctuations in both studies are similar, the reasoning for the change is conflicting. Sun *et al.* (2004a) conclude that the change in fur seal hair abundance correlates with warmer periods whereas fluctuations at South Georgia correlate with cooler periods (see section 5.8.3). This conflict can be explained using a model of optimum sea ice conditions as outlined by Smith *et al.* (1999).

## 5.11 Optimum sea ice conditions hypothesis

Smith *et al.* (1999) suggest krill populations are closely correlated to sea ice distribution, therefore, are affected by climate change. From a study of adélie penguins, the optimum level of krill availability is thought to be between two extremes of sea ice cover; excessive and insufficient ice cover. Depending upon the location of the breeding sites, the penguin population can increase and decrease at two different locations during the same period of time (see figure 5.13).

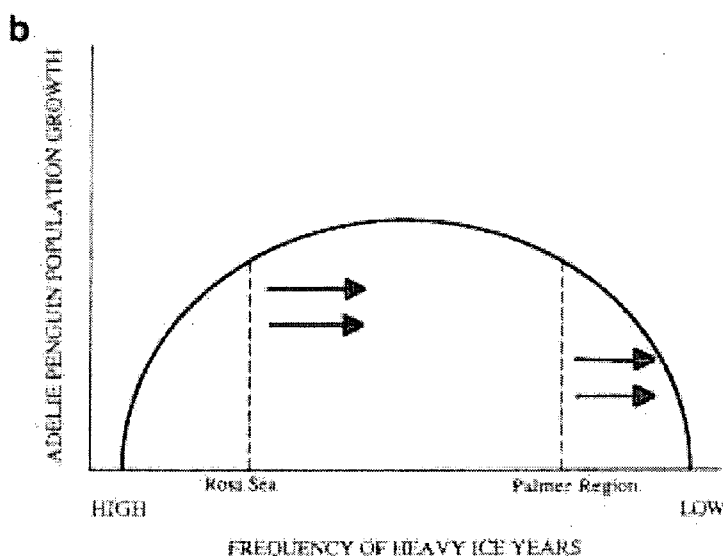


Figure 5.13: Conceptual model indicating the direction of Adélie penguin population changes in relation to sea ice extent (source Smith *et al.* 1999). This model highlights that in years of lower sea ice cover, populations of Adélie penguins in the Ross sea increase, whereas they decrease in the Palmer region.

Relating this model to fur seal populations, the population at South Georgia is near the limit of present day sea ice extent (see figure 5.12) therefore, any decrease in temperature increases the sea ice extent and hence, increases prey availability (Hansom and Gordon 1998; Smith *et al.* 1999). Using this hypothesis, it can be inferred that due to the positive correlation of fur seal population and prey availability, (as discussed in section 2.7.4) the fur seal population will increase at South Georgia during cooler periods.

King George Island is an island in the South Shetland Islands, located at 62°S and 59°W, 12° further south than South Georgia and therefore experiences a cooler climate (see figure 5.12). Recent temperature data suggests that the annual average temperature is approximately 2°C cooler than South Georgia and the extent of sea ice is within 200km of the islands, in comparison to 800km from South Georgia (see figure 5.12) (Boveng *et al.* 1998; [www.antarctica.ac.uk/met/READER](http://www.antarctica.ac.uk/met/READER)). A warming in the region would reduce sea ice extent hence, decreasing the proximity of sea ice to South Georgia and increasing it relative to the South Shetland Islands. A cooling in the region would increase the proximity of sea ice boundary relative to South Georgia. As discussed in chapter 2, sea ice extent is a key factor in the survival of the fur seal. As climate changes are described in relative terms, rather than actual terms, a cooling in South Georgia and a warming in the South Shetland Islands may result in similar temperatures, and therefore explain the difference in results from South Georgia and the South Shetland Islands.

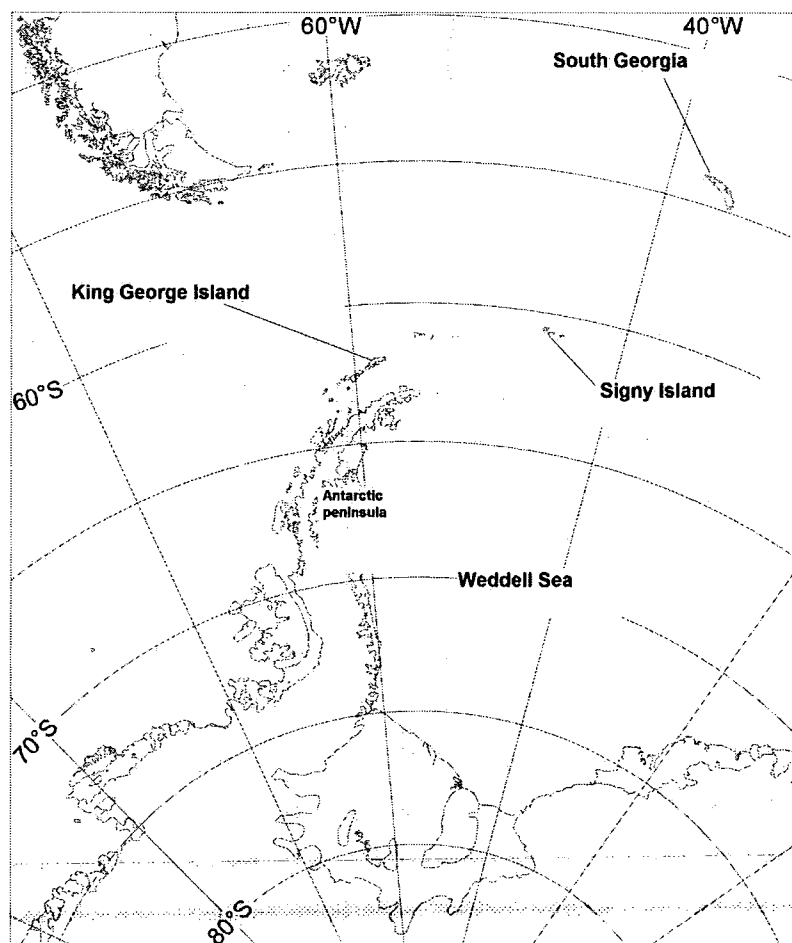


Figure 5.14: The location of Signy Island and King George Island in relation to South Georgia.

Figure 5.15 shows an adaptation of figure 5.13 to suit fur seal populations in the Sub Antarctic Islands. Line A illustrates the situation during a warmer period (relative to today), therefore, the number of fur seals on South Georgia decreases as the sea ice extent reduces and prey availability declines. On King George Island, as sea ice declines, the boundary of the sea ice extent moves closer to King George Island and therefore, prey availability rises hence, increasing fur seal populations. During a cooler period (relative to today) the situation is shown in line B. As sea ice extent increases at South Georgia prey availability increases, therefore, the fur seal population at South Georgia grows. However, the sea ice extent is too great at King George Island for optimum levels of prey availability hence, the fur seal population decreases.

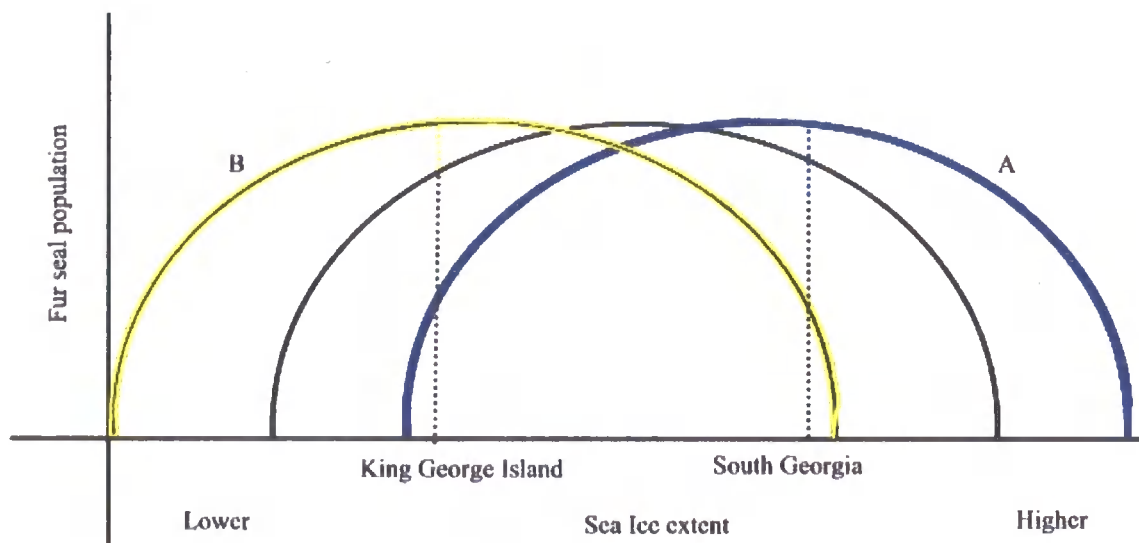


Figure 5.15: Conceptual model illustrating fur seal population changes in relation to sea ice extent (adapted from Smith *et al.* 1999). The black line is an approximation of the situation today, although the exact magnitude and position of the islands cannot be determined with the available data. Line A (blue line) indicates a climate relatively cooler than today. Line B (yellow line) indicates a climate relatively warmer than today.

Although this model may not explain all the variation in the record, it does clarify the general trend and agrees with the conclusion that fur seal population fluctuations are intimately related to sea ice distribution. Details in the fur seal hair abundance record however, are not accounted for in this figure and it does not explain the greater fluctuations in the fur seal population at King George Island compared to South Georgia. On King George Island, fur seal populations decline rapidly between peaks,

whereas at South Georgia the population is continually increasing from a minimum at the base of the core. However, larger peaks occur at South Georgia at a similar time to those on King George Island therefore, it is possible that a larger population at South Georgia can be sustained as a consequence of more favourable environmental conditions and predator relationships. As a larger population can be sustained, the climate variability does not affect the fur seals as significantly as at King George Island and hence, population decline is not as evident in the record.

#### 5.11.1 20<sup>th</sup> Century changes

Although the model outlined in figure 5.15 correlates with changes in the fur seal population during the late Holocene, it cannot be applied to 20<sup>th</sup> century changes in the fur seal population as the population is increasing during a period of warming, opposite to the trend modelled in figure 5.15. Figure 5.16 shows an adapted model of figure 5.15 to incorporate 20<sup>th</sup> century changes. The blue line shows the potential fur seal population during the 20<sup>th</sup> century under krill surplus conditions, when the potential fur seal population is greater. The magnitude of this is unknown and cannot be evaluated until the fur seal population begins to decline at South Georgia, as indicated at point A in figure 5.16. Once this threshold has been reached and the krill availability is no longer sufficient to sustain the fur seal population, the fur seal population will decline at South Georgia. On King George Island however, the population may continue to increase due to the warmer climate conditions.

The situation today is not known exactly but is located on the line between points A and C as it is known that a krill surplus effect exists (Croxall *et al.* 2002). The results of the fur seal hair abundance suggest that the fur seal population today is not greater than the population during the late Holocene; therefore, it is likely that the population is located between points B and C. Due to the resolution of the core, this is not known exactly (see section 5.2.3) therefore, it is possible that the population today has exceeded the optimum fur seal capacity of the Southern Ocean prior to the krill surplus hence, the population *may* be at a point between point A and B. Once point A is reached, i.e. the krill surplus effect is no longer effective at South Georgia and it is likely that the fur seal population will begin to decline.

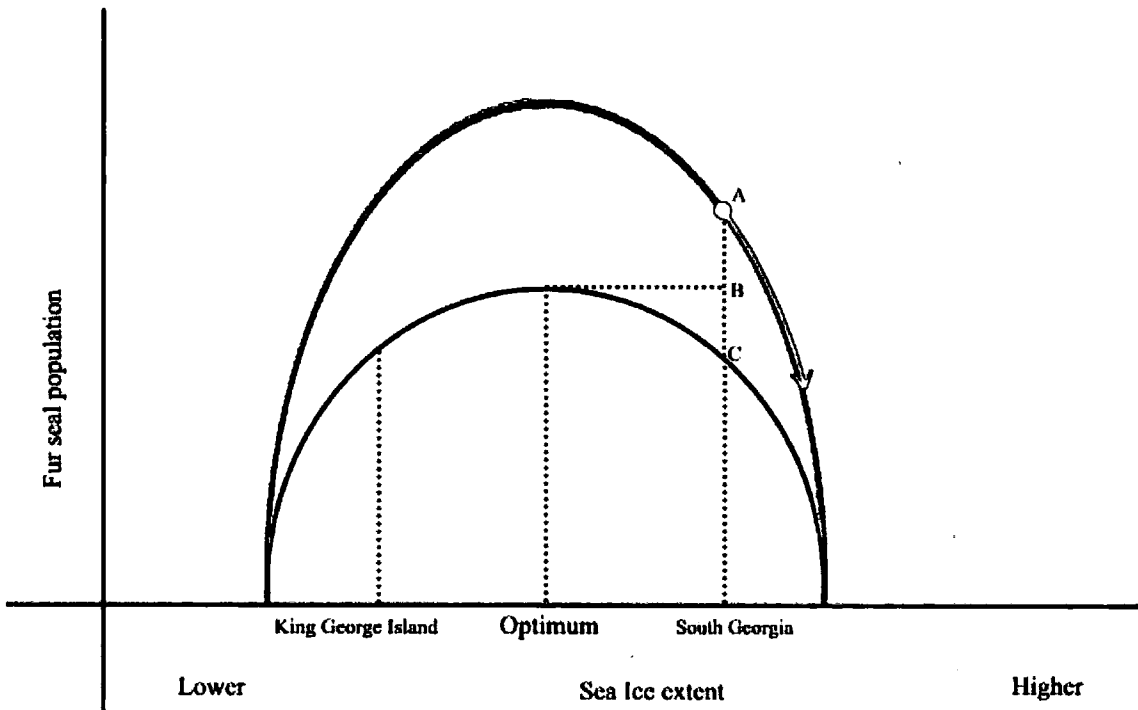


Figure 5.16: Conceptual model of fur seal population changes in relation to sea ice extent and prey availability as a result of the krill surplus effect during the 20<sup>th</sup> century. The black line indicates the fur seal population in relation to sea ice conditions prior to a krill surplus; the blue line indicates the fur seal population in relation to sea ice conditions during a period of krill surplus.

### 5.11 Summary

The above discussion suggests that the fur seal populations on South Georgia, and in the sub-Antarctic region as a whole are influenced primarily by krill availability, both during the late Holocene and during the 20<sup>th</sup> century. However, the mechanisms causing the change in krill availability has varied, from natural environmental change pre 200 yrs BP to human induced changes post 200 BP. The implications of this in terms of predicting future changes and implementing management measures will be addressed in the following chapter.

## Chapter 6

### Conclusions



Plate 6: Fur seals and penguins on the beach at Maiviken, South Georgia.

## 6 Conclusions

This chapter outlines the main conclusions of this thesis and is structured using the objectives discussed in chapter 1.

6.1 Objective 1: To reconstruct fur seal populations through the late Holocene by counting seal hairs from a lake on South Georgia.

Using fur seal hair abundance as a proxy for fur seal populations, allows an indication of the fluctuations and magnitude of the population through the core. From this record, it can be inferred that the fur seal population on South Georgia has been present for at least the past 3439  $^{14}\text{C}$  yrs BP. At the beginning of the record (3439  $^{14}\text{C}$  yrs BP) the fur seal population at South Georgia was the lowest it has been for the past 3439  $^{14}\text{C}$  years. From this minimum, the fur seal hair abundance record suggests the population increased and plateaued at a level approximately 4000 hairs per 1 g of dry weight (see figure 5.2). Although the population increased beyond this level, peaks were brief and only lasted c. 300 years before declining back to previous levels.

6.2 Objective 2: To reconstruct fur seal populations indirectly using geochemical analysis, following the method outlined by Sun *et al.* (2004a).

At South Georgia, none of the elements tested for can be used to reliably reconstruct the fur seal population during the past 3439  $^{14}\text{C}$  yrs BP. Zinc and copper are the most closely correlated to fur seal hair abundance however, the fur seal signature is only seen when the population reaches a threshold of 1500 hairs per 1 g of dry weight. Other elements such as carbon and nitrogen correlate with the fur seal population when the catchment is stable. However, a large catchment change occurs at approximately 3000  $^{14}\text{C}$  yrs BP, increasing the concentration of carbon and nitrogen, obscuring the fur seal signature in this record.

On South Georgia, the fur seal signature is not as evident in the geochemistry as in previous studies, this can be attributed to factors such as catchment stability, vegetation cover and seal populations. Evidence presented in this study suggests that the elements highlighted by Sun *et al.* (2004a) as bio indicators for fur seal population are not

transferable from one catchment to another as each catchment displays different characteristics such as biological composition, climate conditions and lake circulation. For example, at South Georgia, tussock grass is abundant in the catchment, and affects the chemical composition of the lake sediments, in areas where this is not as abundant, such as King George Island, the fur seal signature is likely to be more pronounced.

6.3 Objective 3: To determine whether the recent (20<sup>th</sup> –21<sup>st</sup> century) increases in fur seals have exceeded the range of natural variability of past populations.

Due to the unexpectedly low resolution in the top part of the core and the  $^{210}\text{Pb}/^{137}\text{Cs}$  dating problems, evaluating the 20<sup>th</sup> and 21<sup>st</sup> century changes in the population is difficult. In this thesis I assume that the core top is equivalent to 0 yrs BP (reasons for this are outlined in section 5.2.3). If this is correct then the fur seal population during the 20<sup>th</sup> and 21<sup>st</sup> century does not appear to be significantly higher than at any time during the past 3439  $^{14}\text{C}$  yrs BP.

In addition to the actual size of the population, the rate of the fur seal population increase at South Georgia during the 20<sup>th</sup> century is a cause for concern (see section 2.5). During the 20<sup>th</sup> century, the population has increased c.  $10^5$ - $10^6$  times in 100 years (see figure 2.17). As section 5.4 outlines, increases of a similar magnitude are observed through the late Holocene. Figure 5.2 highlights that the fur seal population growth has been greater than growth today at two separate points through the core. Firstly, when the population was at a minimum, as observed at the base of the core, the population increased 10 fold. Secondly; once the population reached a threshold (4000 hairs per 1g of dry weight), if it increased beyond this level, increases were dramatic but brief before the population declined back to similar levels. Using these two hypotheses, 20<sup>th</sup> Century increases in the fur seal population are not unprecedented through the Late Holocene and are expected as the population is recovering from almost extinction at the beginning of the 20<sup>th</sup> Century.

6.4 Objective 4: To review and assess the impact the environmental changes on South Georgia have had upon seal populations over the same time period of the Holocene.

The largest peaks in fur seal population occur during periods of climate deterioration at South Georgia (see figure 5.11). However, studies on other sub-Antarctic islands (e.g.

King George Island) correlate increases in fur seal populations with warming (Sun *et al.* 2004a). This apparent paradox can be explained by analogy using a model correlating penguin populations and sea ice extent as outlined by Smith *et al.* (1999) (see figure 5.13). From past research (see section 2.7.4), the primary controls upon the fur seal population are prey availability and predator competition. Prey availability is strongly controlled by the distribution of sea ice. The zone of optimum sea ice conditions for krill availability and hence, fur seal population growth today is located between King George Island and South Georgia. Although the oceanography of the Southern Ocean is complex and not fully understood, the general principle is that during a cooling these optimum conditions migrate closer to South Georgia, whereas during a warmer period, they migrate closer to King George Island. As krill populations closely follow the sea ice distribution, this movement of sea ice, alters the krill availability and hence, the prey availability for fur seals (see figure 5.15).

It is widely documented that relative to the late Holocene climate, the 20<sup>th</sup> Century was a period of warming. Census data shows the fur seal population has increased during this period in contrast to the palaeo record where populations augment during cooling periods. Using this theory, it can be inferred that the increase in 20<sup>th</sup> century fur seal populations are not a result of natural environmental changes. As 20<sup>th</sup> century changes in the fur seal population are not related to natural environmental changes, the changes must be a consequence of human-induced factors. The most likely human induced cause is the whaling industry that resulted in a krill surplus in the Southern Ocean. This surplus increased the krill availability for fur seals, providing the same effect as increasing sea ice extent, leading to population growth. The effects of this on seal populations were particularly spectacular due to the preceding exploitation of seals to near extinction.

6.5 Objective 5: To determine the factors controlling fur seal population changes at South Georgia through the late Holocene.

From this evidence, the primary control on the fur seal population through the late Holocene is prey availability. Prior to human intervention, prey availability was controlled by sea ice distribution and hence, climatic fluctuations. During the 20<sup>th</sup> century, although the climate conditions do not suggest an increase in prey availability at South Georgia, human intervention caused an artificial increase. In this way this

study confirms the assertions by Croxall (1992) that the krill surplus has been the primary driver for 20<sup>th</sup> century fur seal population increases on South Georgia.

## 6.6 Overall aim

My aim was to reconstruct the fur seal population of South Georgia by counting seal hairs from a South Georgia lake sequence as a proxy for fur seal abundance combined with geochemical analysis using techniques outlined by Hodgson *et al.* (1998) and Sun *et al.* (2004a). Comparing the population fluctuations in 20<sup>th</sup> century and late Holocene fur seal populations allowed the controlling factors underlying fur seal population fluctuations to be better understood and hence, aid management and conservation decisions.

As figure 5.2 shows, the fur seal population has been reconstructed from fur seal hair abundance. The use of geochemical analysis for reconstructing the fur seal population in this study has not proved successful and has highlighted the problems in transferring geochemical signatures between catchments. Although the 20<sup>th</sup> century population cannot be precisely compared with late Holocene population fluctuations due to the resolution of the core, assuming that 0 cm is 0 yrs BP, the 20<sup>th</sup> century changes are not unprecedented. The factor controlling these fur seal population changes through the past 3439 <sup>14</sup>C yrs BP has been primarily prey availability, influenced by sea ice and hence, climate changes before human intervention. As krill populations during the Late Holocene are only estimates, the magnitude of the krill increase during the 20<sup>th</sup> century cannot be accurately quantified, however, it is widely recognised that the krill population has increased during the early 20<sup>th</sup> century due to the krill surplus effect. This artificial increase in prey availability as a result of human intervention has caused a consequent increase in the fur seal population.

In term of addressing the management issues associated with the fur seal population at South Georgia (see section 2.8.1), evidence from this study suggests that management may not be necessary. The fur seal population at South Georgia through the Holocene was at levels as high if not higher than the fur seal population today. Following a large increase, the fur seal population returned back to previous levels as part of the natural cycle. Although the actual trigger for 20<sup>th</sup>-21<sup>st</sup> century increases in population was not

part of the natural cycle, there is strong evidence to suggest the mechanism by which it occurred (prey availability) as the same.

### 6.7 Future change in the fur seal population at South Georgia

As the factor controlling the fur seal population (prey availability) is the same through the late Holocene, it is clear that this increase cannot be maintained once prey availability reaches a threshold. Once the krill surplus period ceases, the prey availability will reduce and it is likely that the fur seal population will decline (see figure 5.16). I predict that the fur seal population will cease to increase and the population will plateau at a level equivalent to the deposition of ~ 4000 hairs per 1 g of dry weight. This estimate however, is based upon evidence from past natural environmental change and the impact of human induced changes may be more extensive than initially thought. For example the effect of climate phenomena such as El Niño on the fur seal population has not been assessed in this study. As Croxall *et al.* (2002) highlight, El Niño affects sea ice processes in the Southern Ocean. The effect on the krill population is not fully understood and therefore, to comprehend factors affecting fur seal populations, the mechanisms affecting sea ice distribution and krill distribution must first be fully comprehended. In addition to this, human impacts on the krill population such as the growth of krill fisheries or a change in location of the krill fisheries will cause fluctuations in krill populations independent of natural long-term climate changes (Croxall and Nicol 2004).

### 6.8 Summary

The fur seal population at Maiviken, South Georgia has been present for at least 3439  $^{14}\text{C}$  years BP. Increases in the population are the most rapid when the population is very low or during colder periods however, fur seal hair abundance plateaus at approximately 4000 hairs per 1 g of dry weight. Although increases are documented above 4000 hairs per 1g of dry weight, these increases cannot be maintained for a sustained period of time.

The primary factor influencing the fur seal population at South Georgia is prey availability; hence, indirectly the mechanisms causing changes in prey availability affect fur seal populations. Through the past 3439  $^{14}\text{C}$  years BP there has not been a

time when the krill population at South Georgia has declined significantly enough to cause extinction of the fur seal population. Prior to human intervention, prey availability was primarily controlled by sea ice distribution and hence, climate changes. During the 20<sup>th</sup> and 21<sup>st</sup> century the primary factors affecting prey availability have been human induced changes which have resulted in a krill surplus. Despite this, once such a surplus ceases or the population reaches a threshold, the population will stop growing and it is likely that the population will stabilise or decline.

Highlighting prey availability as the cause of fur seal population growth has improved understanding of fur seal population fluctuations and the impact that human-induced changes has upon these populations. Such findings can then be used to aid management and conservation decisions. Correlating fur seal populations with sea ice distribution has improved the understanding of the factors controlling fur seal populations; hence, past fur seal populations could potentially now be used as an important indicator of environmental change in the sub Antarctic region (Jouventin and Weimerskirch 1990).

## Chapter 7

### Limitations and Further Research



Plate 7: Fur seals in tussock grass

## 7 Limitations and Further Research

In light of the findings of this study as outlined in the previous chapter, it is important to note that there are a number of limitations inherent in a study of this nature, not least clear restraints of time and logistics. For this reason I shall examine these limitations below and the avenues that such shortcomings may open for future research before finally looking towards their relation to the projects overall outcomes.

### 7.1 Dating

#### 7.1.1 $^{210}\text{Pb}$ dating

As the  $^{210}\text{Pb}$  dating technique was unsuccessful, the top section of the core was dated using a constant sedimentation rate calculated from radiocarbon dates deeper in the core. This technique incurs a larger potential error in the dates at the top of the core and therefore, the fluctuations noted in fur seal hair abundance during the 20<sup>th</sup> century cannot be accurately determined and compared relative to the timing of the sealing and whaling activity. As a consequence of this, the impact of human induced changes cannot be as accurately evaluated as other studies have done (Hodgson *et al.* 1998). Inaccurate dating in the top section of the core has also prevented the census data and fur seal hair abundance being compared and hence, the development of a transfer function which would allow the size of the fur seal population prior to exploitation to be quantified.

#### 7.1.2 Radiocarbon dating

The radiocarbon dates obtained from the core show a reversal at the base of the core (see section 5.1), as a result only two radiocarbon dates were used to date the whole core. In addition to this, the top radiocarbon date was unexpectedly old resulting in the resolution of the hairs in the top section of the core to be very low. Obtaining the radiocarbon dates before calculating seal hair abundance would have allowed a greater sampling resolution to be taken in the top section of the core and therefore, allowing the time- stratigraphic sampling resolution to be continuous through the core. Alternatively, if time had allowed, organic fragments in the sediment could have been extracted and dated separately to determine the potential ageing effect of old carbon in the sediment.

Although this is dependant on fragments being present in the sediment, using this aging factor, the dates radiocarbon obtained could have been corrected. Furthermore, as the sedimentation rate at the top of this core was so low, an alternative core with a higher sedimentation rate could have been used to reconstruct the fur seal population, hence, providing a more accurate record of change during the 20<sup>th</sup> century which could be compared to census data.

## 7.2 Fur seal hair abundance

Although calculating fur seal hair abundance provides a useful indicator of fur seal presence, it does have its limitations that must be considered when analysing the data.

### 7.2.1 Human error

The method used to count fur seal hairs as this study demonstrates can incur a large amount of error (see section 3.6) even using the same method of preparation and with the same person counting. This presents problems in comparing the data from one site to another and hence, developing a transfer function which could be used to quantify the fur seal population.

### 7.2.2 Population dynamics

Although using fur seal hair abundance as a proxy for fur seal populations provides an indication of the size of the fur seal population, the population dynamics and interactions with the ecosystem cannot be deduced from this method thus, causing difficulties in determining factors affecting past populations. A decline in fur seal hair abundance implies a decline in the population however; it is possible that a decline in fur seal hairs was a result of population migration due to a change in the localised conditions rather than a system change such as a regional decline in krill or a climatic change. Although this is reflected in the geochemical data, further cores from other catchments would help to distinguish these localised changes from a large system shift on South Georgia.

Furthermore, factors affecting the fur seal population historically may not affect the population today due to evolution and the ability of the fur seal to adapt to differing conditions. An example of this is a change in the prey availability; from recent research,

the primary prey of the fur seal at South Georgia is krill and research indicates that the foraging behaviour of the fur seal changes to accommodate changes in prey distribution and abundance (Green *et al.* 1989; Reid and Arnould 1996; Boyd *et al.* 1994). Although this is the case today, it is possible that past populations of fur seals were not as well adapted, therefore, smaller more localised changes in prey abundance would have a greater impact upon the population. Natural changes in prey availability in the past may appear as a larger natural change than actually occurred due to the ability of the fur seal to adapt to system changes, hence, comparing the magnitude of historical fur seal population changes with changes today and inferring possible mechanisms for this change has limitations.

### 7.3 Areas of further research

This was a time-limited study and there are obviously a number of potential avenues remaining for future research

#### 7.3.1 Radiocarbon dates

Two of the radiocarbon dates were obtained after the fur seal hair abundance had been assessed. Collecting these dates earlier in the study would have allowed the core top to be sampled at a higher resolution based upon the age- stratigraphy rather than depth-stratigraphy. Alternatively a core with a higher sedimentation rate at the core top could have been analysed. A higher sampling resolution at the top of the core would have allowed the 20<sup>th</sup> century changes in the fur seal population to be assessed to a greater extent, therefore, allowing a more exact assessment of whether 20<sup>th</sup> century increases in the population had occurred previously during the late Holocene.

#### 7.3.2 Dating 'old' carbon

To determine the potential ageing effect of the carbon on the sediment, visible organic fragments could be extracted from the sediment and radiocarbon dated separately. This would provide an indication whether there has been significant sediment reworking. Using this date, it may be possible to determine the dating error and provide a better indication as to which radiocarbon dates are more accurate.

### 7.3.3 Palaeocological analysis

To provide a baseline for the radiocarbon dates and hence, provide a greater indication of the accuracy of the dates, palaeocological analysis could be implemented at key sediment transitions. Although Troels – Smith analysis (see section 4.1) indicates uniform sediment for the majority of the core, the basal section of the core could be analysed to determine when this sediment change took place and related to other proxy records to determine the age of this key sediment change. Determining the cause of the sediment change would also help to evaluate the accuracy of the radiocarbon dates obtained and hence, provide a more robust age model.

### 7.3.4 Additional cores

As two separate cores were used (MAIVK and HUM3), there is a gap in the record. Although this c.10 cm gap is relatively small, the exact size is unknown. During extraction, the position of the cores in relation to each other was calculated however, in the field it is difficult to measure this difference accurately. At the time of coring an additional core was extracted from the same point, covering this gap between MAIVK and HUM3. Using magnetic susceptibility the cores could be aligned and allow the size of the gap to be calculated accurately. This would allow the section of the sediment to be analysed for fur seal hair abundance and geochemistry, hence, providing a fully continuous record of fur seal hair abundance for the past 3500 years.

In addition to improving the core at the single study site, additional cores could be analysed from other sites on South Georgia. The study of additional cores would broaden the project and allow a further insight into fur seal population dynamics through the Holocene. Potential sites for additional cores include those that could aid an understanding of the expansion of the seal population both altitudinally and along the coast of South Georgia as illustrated below.

Proposed sites for additional cores:

- a. Altitude

Lewis-Smith (1988) highlights slopes of 200 metres altitude are now being threatened by fur seals at South Georgia. This is a higher altitude than any time previously during the 20<sup>th</sup> century however, it is unknown whether fur seals have reached this altitude previously during the Holocene (pre 1900), when census data is not available. Taking further cores from higher altitudes would provide an insight as to whether this situation occurred previously and whether the environment can recover from such an event. It would also provide an indication of the maximum fur seal population the area can accommodate. For example, if the population has previously reached similar levels to today but not gone beyond this level, it may indicate that the carrying capacity of this location has been reached. In order to assess the maximum level that fur seals have reached additional study sites are needed at the altitudinal limits of the fur seal breeding range.

b. Bird Island

Bird Island is the main breeding ground for the fur seal at South Georgia; therefore, the impact is the most pronounced. The first pup observed on South Georgia following the sealing and whaling industries was on Bird Island (Payne 1977). As this was the first site, the exact timing of the recovery of the fur seal population can be calculated. Census data indicates that the population growth migrated from Bird Island, therefore, population growth at Maiviken was delayed and the exact timing and causal mechanism for this growth cannot be assessed accurately. Comparing the timing of changes in fur seal abundance at Bird Island with changes on the mainland allows the rate of the expansion to the mainland of South Georgia to be determined hence, the optimum carrying capacity of Bird Island can be measured to aid in management decisions.

Due to the high population of fur seals on Bird Island, the fur seal census data of Bird Island is the most accurate and extensive for the whole of South Georgia. This detailed census data for the 20<sup>th</sup> century allows the number of fur seals to be accurately correlated with the fur seal hair abundance, therefore, the number of fur seals during the Holocene can be quantitatively assessed through a transfer function.

c. Latitudinal transect

The fur seal population has migrated from a small colony on Bird Island to the main island. Taking cores along a transect from Bird Island to the south of the main island and reconstructing the fur seal population would allow the rate of migration and the impact this has had upon the environment to be assessed. A visual assessment of the environmental conditions at each site compared relative to the fur seal population allows a greater understanding of the management measures required.

#### 7.4 Continuing previous research

##### 7.4.1 Sediment traps

Hodgson *et al.* (1998) used sediment traps in the lake to calculate the number of hairs trapped within the lake and the amount of mixing that occurred in the lake itself. In the traps, the number of hairs collected were calculated and used to indicate the trapped hair that would be incorporated into the sediment at different times of the year.

Although I assumed the results of this study could be applied to the lake at South Georgia, as the results from the geochemical analysis highlight (see section 4.4.7), different catchments display different characteristics and therefore, it is likely that the situation as observed in the Hodgson *et al.* (1998) study is not representative of the lake at South Georgia. This affects the results of the fur seal hair abundance; firstly sediment traps allow the mixing of the lake to be calculated, therefore, allowing the best position for the cores to be taken and facilitating the most accurate measure of fur seal hair abundance. For example, the coring site in this study may be a site that is particularly abundant in fur seal hairs at the time of coring due to the flow within the lake. Taking sediment traps allows an assessment of the flow within the lake, thereby preventing a core being taken from a site not typical of the lake or if the core is taken in a section of the lake that is not representative of the lake as a whole, it allows for a correction in the results.

##### 7.4.2 Geochemical analysis

Following Sun *et al.* (2004a), I used geochemical analysis to evaluate elements that could be used as potential bio indicators of fur seal presence. Unfortunately, due to the shortage of sample and the restrictions on instruments, fluorine and phosphorous, (found by Sun *et al.* (2004a, b) to be indicators of fur seal and penguin populations)

could not be tested for. Analysing the similar elements as Sun *et al.* (2004a), allowed the transferability of the bio element indicators at one site to be assessed. Although this can be done to some extent, as a number of the elements Sun *et al.* (2004a) tested for were also tested for in this study, it is still possible that the elements not tested for were the most indicative of fur seal presence. With additional time and sample size these additional analyses could be implemented.

#### 7.4.3 Wider research issues

The above issues are possible study areas to explore if the time were available however, the issues outlined below are larger and wider ranging issues beyond the scope of an individual study but should be noted as important issues that would enhance the results of this study.

##### 7.4.3.1 $^{210}\text{Pb}$ and $^{137}\text{Cs}$ problems

To date there are few palaeolimnological studies at South Georgia that have successfully used  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  dating (see section 5.2). Unpublished data suggests previous studies have experienced problems in detecting low concentrations of  $^{210}\text{Pb}$  in lake sediments (Rosqvist, G. pers. comm.). This apparent lack of  $^{210}\text{Pb}$  may be isolated to this particular core due to loss of sediment or the lack of sediment used for detection (see section 5.2.1 for further explanation), but as there have been no other studies that have dated South Georgian lake sediments using  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  successfully, it appears to be an island wide problem. To fully assess this issue, further lake cores are needed from a variety of locations across the island. The use of a variety of detectors and sizes of sediment samples will also help to evaluate the cause of the lack of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the core.

##### 7.4.3.2 Isotopes in hair

It is widely recognised that carbon and nitrogen isotope signatures can be used to trace food webs and understand palaeodiets in terrestrial and marine ecosystems (Lajtha and Michener 1994). The isotopic composition of food and fluids ingested by animals has a strong influence on the isotopic composition of their tissues. As carbon and nitrogen isotopes fractionate in a predictable way between each trophic level the isotopic composition reflects the trophic position of the animal (Koch *et al.* 1994; Hobson *et al.* 1996). In this way, measuring the isotopic composition of animal tissue provides an

indication of their position in the food web and hence, their diet. Using this theory, it is possible that isotopes in fur seal hair can be used to trace palaeodiet through the Late Holocene

Carbon is fractionated by 3 primary processes; firstly preferential loss of  $^{12}\text{C}$  during respiration, secondly preferential uptake of  $^{13}\text{C}$  compounds during digestion and thirdly metabolic fractionation during synthesis of different tissue types. This fractionation results in an enrichment of  $^{13}\text{C}$  by 1.1‰ at each trophic level (Michener and Schell 1994; Rau *et al.* 1983). This carbon isotopic signature can be used to determine the marine domain in which an animal is obtaining its prey, for example,  $\delta^{13}\text{C}$  values are higher in nearshore food webs than in offshore food webs (Kurlle and Worthy 2001).

Nitrogen isotopes are also fractionated during biological processes and therefore, can be used as a tracer for dietary analysis and to determine the trophic level of given animals (Minagawa and Wada 1984). Faure (1986) suggests that animal tissue is enriched in  $^{15}\text{N}$  relative to dietary inputs and therefore, an average enrichment of 3.0‰ of  $^{15}\text{N}$  is observed at each trophic step (Faure 1986; Zhao *et al.* 2004). This enrichment of  $^{15}\text{N}$  with each trophic step allows the position of the animal in the food chain to be assessed (Kelly 2000).

Isotopic fractionation and the assessment of trophic positions in food webs has been used in previous studies to provide an insight into whether modern pinniped populations change in relation to human influences on the marine ecosystem or in response to longer oceanographic or climatic changes (Burton and Koch 1999). Previous studies of Antarctic Seals have indicated that Weddell Seals occupy a higher trophic position than Ross seals and are considered the top predator in the Antarctic phocid ecosystem (Zhao *et al.* 2004). Calculating the isotopic composition of fur seals and comparing the carbon and nitrogen isotopic ratios with other seals in the region, will allow the fur seal competition for prey to be evaluated.

As Burton *et al.* (1999) highlight this method of determining the trophic position of seals can also be used to determine the cause of historic population changes. As Hobson *et al.* (1996) indicate, analysis of metabolically inactive tissues such as hair, skin, whiskers, nails and feathers reflect the diet of individuals during the period of growth. Using this theory, the isotopic ratios in hairs through the core could be used to assess

the changes in the trophic relationships of the Antarctic fur seal through the Holocene. This would provide an indication of the influence prey availability has upon the fur seal population, which can be used to assess the impact human induced changes and natural environmental change have had upon the 20<sup>th</sup> and 21<sup>st</sup> century increases in populations.

#### 7.4.3.3 Sea ice conditions

De la Mare (1997) highlights the possibility of reconstructing the sea ice boundary of the Southern Ocean during the 20<sup>th</sup> century from whaling records. As fur seal populations correlate with krill distribution and therefore sea ice extent, a similar principle can be used to reconstruct sea ice extent during the late Holocene using fur seal hair abundance records. As I have highlighted in section 5.11, with the record from only two islands (South Georgia and King George Island), an indication of the sea ice extent can be inferred. Reconstructing the fur seal population on a range of islands in the sub Antarctic region would allow this to be more fully understood and therefore, enhance understanding of the factors this affects such as productivity and oceanic circulation. Such a move will also help to comprehend climate changes and the possible impacts this has upon other species. For example, as Croxall *et al.* (2002) highlight, adélie penguins and emperor penguins are closely related to sea ice distribution, therefore, reconstructing sea ice distribution through the late Holocene would provide an indication of their distribution in the Southern Ocean through the late Holocene.

### 7.5 Summary

Despite the limitations outlined in this chapter there are a number of important outcomes to emerge from this study that can be taken forward in future research. As I have discussed, dating the core restrained the scope of this study as the 20<sup>th</sup> century changes in fur seal hair abundance could not be accurately compared to Late Holocene population fluctuations, therefore, it cannot be accurately assessed whether 20<sup>th</sup> century population growth is unprecedented during the late Holocene. Despite this, an important outcome of the study is the correlation between fur seal population growth, sea ice extent and the reliance of the fur seal population upon krill availability. From this correlation, as fur seal populations during the 20<sup>th</sup> century are increasing during a warming period, it can be deduced that population changes at this time are not a result of natural environmental changes. As a result, it can be concluded that 20<sup>th</sup> century population increases are a consequence of human induced changes, primarily a result of

the krill surplus. This linkage can be used to predict future population shifts thereby aiding important decisions for future management and conservation of the Antarctic fur seal population both at South Georgia and the Southern Ocean.

## Appendix 1

### Fur seal hair counts

These are the counts of fur seal hair abundance expressed as number per 1 g of dry weight. Each sample was counted 3 times however as the first count (count a) was significantly higher, only the second and third counts (count b and count c) are used in analysis. Sample depth is the actual sample number without correction for core shrinkage, actual depth is the depth in the core after correction for shrinkage using equation 3.1 outlined in section 3.1.1. SD is the standard deviation of the counts for each sample. Average SD is the average of the standard deviations for each individual sample, which is used as the error in the data.

| 14C yrs BP | Sample Depth | Actual depth | Count a | Count b | Count c | Average (all counts) | Average (2nd+3rd count) | Average SD (all counts) | Average SD (2nd + 3rd count) |
|------------|--------------|--------------|---------|---------|---------|----------------------|-------------------------|-------------------------|------------------------------|
| 0.00       | 0            | 0            | 6172.7  | 3045.5  | 2390.9  | 3869.70              | 2718.18                 | 1650.27                 | 327.27                       |
| 110.00     | 2            | 2.6          | 7108.3  | 6666.7  | 4416.7  | 6063.89              | 5541.67                 | 1178.64                 | 1125.00                      |
| 220.00     | 4            | 5.3          | 3670.0  | 3090.0  | 2240.0  | 3000.00              | 2665.00                 | 587.25                  | 425.00                       |
| 330.00     | 6            | 7.9          | 9190.0  | 3800.0  | 4120.0  | 5703.33              | 3960.00                 | 2468.90                 | 160.00                       |
| 440.00     | 8            | 10.6         | 9570.0  | 5820.0  | 4270.0  | 6553.33              | 5045.00                 | 2224.98                 | 775.00                       |
| 550.00     | 10           | 13.2         | 11463.6 | 5500.0  | 4390.9  | 7118.18              | 4945.45                 | 3105.88                 | 554.55                       |
| 660.00     | 12           | 15.9         | 15120.0 | 5530.0  | 3530.0  | 8060.00              | 4530.00                 | 5058.50                 | 1000.00                      |
| 770.00     | 14           | 18.5         | 5790.9  | 2554.5  | 2972.7  | 3772.73              | 2763.64                 | 1437.25                 | 209.09                       |
| 880.00     | 16           | 21.2         | 11644.4 | 5500.0  | 2900.0  | 6681.48              | 4200.00                 | 3666.36                 | 1300.00                      |
| 990.00     | 18           | 23.8         | 3310.0  | 2820.0  | 2410.0  | 2846.67              | 2615.00                 | 367.91                  | 205.00                       |
| 1100.00    | 20           | 26.5         | 20600.0 | 9060.0  | 4630.0  | 11430.00             | 6845.00                 | 6731.66                 | 2215.00                      |
| 1210.00    | 22           | 29.1         | 7345.5  | 4663.6  | 2590.9  | 4866.67              | 3627.27                 | 1946.34                 | 1036.36                      |
| 1320.00    | 24           | 31.8         | 7381.8  | 3027.3  | 3390.9  | 4600.00              | 3209.09                 | 1972.64                 | 181.82                       |
| 1430.00    | 26           | 34.4         | 6741.7  | 3350.0  | 3533.3  | 4541.67              | 3441.67                 | 1557.43                 | 91.67                        |
| 1540.00    | 28           | 37.1         | 6207.1  | 3300.0  | 2507.1  | 4004.76              | 2903.57                 | 1590.60                 | 396.43                       |
| 1650.00    | 30           | 39.7         | 4810.0  | 3560.0  | 2980.0  | 3783.33              | 3270.00                 | 763.60                  | 290.00                       |
| 1760.00    | 32           | 42.4         | 3260.0  | 1380.0  | 2230.0  | 2290.00              | 1805.00                 | 768.68                  | 425.00                       |
| 1870.00    | 34           | 45           | 7327.3  | 3227.3  | 3390.9  | 4648.48              | 3309.09                 | 1895.37                 | 81.82                        |
| 1980.00    | 36           | 47.6         | 21355.6 | 7066.7  | 3422.2  | 10614.81             | 5244.44                 | 7739.21                 | 1822.22                      |
| 2090.00    | 38           | 50.3         | 5440.0  | 1830.0  | 6210.0  | 4493.33              | 4020.00                 | 1909.32                 | 2190.00                      |
| 2200.00    | 40           | 52.9         | 6772.7  | 3245.5  | 3581.8  | 4533.33              | 3413.64                 | 1589.43                 | 168.18                       |
| 2310.00    | 42           | 55.6         | 4233.3  | 1475.0  | 2333.3  | 2680.56              | 1904.17                 | 1152.54                 | 429.17                       |
| 2420.00    | 44           | 58.2         | 7535.7  | 4100.0  | 2207.1  | 4614.29              | 3153.57                 | 2205.57                 | 946.43                       |
| 2530.00    | 46           | 60.9         | 7708.3  | 2525.0  | 2316.7  | 4183.33              | 2420.83                 | 2494.00                 | 104.17                       |
| 2640.00    | 48           | 63.5         | 5981.0  | 2136.4  | 2663.6  | 3593.67              | 2400.00                 | 1701.77                 | 263.64                       |
| 2750.00    | 50           | 66.2         | 4160.0  | 2000.0  | 1410.0  | 2523.33              | 1705.00                 | 1182.10                 | 295.00                       |
| 2757.80    | 52           | 68.8         | 6261.5  | 2015.4  | 1900.0  | 3392.31              | 1957.69                 | 2029.40                 | 57.69                        |
| 2765.60    | 54           | 71.5         | 5618.2  | 3927.3  | 1900.0  | 3815.15              | 2913.64                 | 1520.01                 | 1013.64                      |
| 2773.40    | 56           | 74.1         | 11730.0 | 2410.0  | 2350.0  | 5496.67              | 2380.00                 | 4407.70                 | 30.00                        |
| 2781.20    | 58           | 76.8         | 6566.7  | 4166.7  | 1911.1  | 4214.81              | 3038.89                 | 1900.93                 | 1127.78                      |
| 2789.00    | 60           | 79.4         | 7580.0  | 4340.0  | 2320.0  | 4746.67              | 3330.00                 | 2166.55                 | 1010.00                      |
| 2796.80    | 62           | 82.1         | 3927.3  | 3554.5  | 2509.1  | 3330.29              | 3031.80                 | 600.28                  | 522.70                       |
| 2804.60    | 64           | 84.7         | 5030.0  | 2670.0  | 2450.0  | 3383.33              | 2560.00                 | 1167.83                 | 110.00                       |
| 2812.40    | 66           | 87.4         | 3818.2  | 1727.3  | 1481.8  | 2342.43              | 1604.55                 | 1048.32                 | 122.75                       |
| 2816.30    | 67           | 88.7         | 5844.4  | 2355.6  | 1766.7  | 3322.25              | 2061.15                 | 1799.59                 | 294.45                       |
| 2820.20    | 68           | 90           |         |         |         |                      |                         |                         |                              |
| 2849.67    | 0            | 100          | 7314.7  | 1679.4  | 1167.6  | 3387.24              | 1423.51                 | 2784.99                 | 255.91                       |
| 2858.51    | 3            | 103          | 7270.0  | 3540.0  | 4050.0  | 4953.33              | 3795.00                 | 1651.31                 | 255.00                       |
| 2870.29    | 7            | 107          | 6565.2  | 2530.4  | 2182.6  | 3759.42              | 2356.52                 | 1989.08                 | 173.92                       |
| 2882.08    | 11           | 111          | 8980.0  | 3680.0  | 3520.0  | 5393.33              | 3600.00                 | 2537.00                 | 80.00                        |
| 2893.87    | 15           | 115          | 4481.5  | 1511.1  | 1655.6  | 2549.38              | 1583.33                 | 1367.47                 | 72.22                        |
| 2905.65    | 19           | 119          | 6681.8  | 2536.4  | 3090.9  | 4103.03              | 2813.64                 | 1837.48                 | 277.27                       |
| 2917.44    | 23           | 123          | 5473.3  | 1223.3  | 1470.0  | 2722.22              | 1346.67                 | 1947.93                 | 123.33                       |
| 2929.23    | 27           | 127          | 7923.1  | 2438.5  | 1546.2  | 3969.23              | 1992.31                 | 2819.42                 | 446.15                       |
| 2941.01    | 31           | 131          | 1439.7  | 521.9   | 524.7   | 828.77               | 523.29                  | 432.01                  | 1.37                         |
| 2952.80    | 35           | 135          | 4709.1  | 2845.5  | 2281.8  | 3278.79              | 2563.64                 | 1037.22                 | 281.82                       |
| 2964.59    | 39           | 139          | 3245.0  | 640.0   | 721.7   | 1535.56              | 680.83                  | 1209.22                 | 40.83                        |
| 2976.37    | 43           | 143          | 7508.3  | 1083.3  | 1275.0  | 3288.89              | 1179.17                 | 2984.62                 | 95.83                        |
| 2988.16    | 47           | 147          | 4500.0  | 1042.3  | 1323.1  | 2288.46              | 1182.69                 | 1567.99                 | 140.38                       |
| 2999.95    | 51           | 151          | 6744.4  | 2288.9  | 3044.4  | 4025.93              | 2666.67                 | 1946.87                 | 377.78                       |
| 3008.79    | 54           | 154          | 6046.2  | 1965.4  | 1430.8  | 3147.44              | 1698.08                 | 2061.29                 | 267.31                       |
| 3023.52    | 59           | 159          | 6088.9  | 666.7   | 1455.6  | 2737.04              | 1061.11                 | 2391.90                 | 394.44                       |
| 3035.31    | 63           | 163          | 3203.1  | 1387.5  | 1412.5  | 2001.04              | 1400.00                 | 850.06                  | 12.50                        |
| 3047.09    | 67           | 167          | 3833.3  | 1058.3  | 1191.7  | 2027.78              | 1125.00                 | 1277.88                 | 66.67                        |
| 3058.88    | 71           | 171          | 3650.0  | 588.9   | 786.1   | 1675.00              | 687.50                  | 1398.85                 | 98.61                        |
| 3070.67    | 75           | 175          | 4709.1  | 1172.7  | 1181.8  | 2354.55              | 1177.27                 | 1664.92                 | 4.55                         |
| 3082.45    | 79           | 179          | 9109.5  | 985.7   | 981.0   | 3692.06              | 983.33                  | 3830.72                 | 2.38                         |
| 3094.24    | 83           | 183          | 2712.5  | 775.0   | 750.0   | 1412.50              | 762.50                  | 919.30                  | 12.50                        |
| 3106.03    | 87           | 187          | 4043.5  | 1230.4  | 1187.0  | 2153.62              | 1208.70                 | 1336.45                 | 21.74                        |
| 3117.81    | 91           | 191          | 3814.3  | 2700.0  | 2228.6  | 2914.29              | 2464.29                 | 664.86                  | 235.71                       |
| 3129.60    | 95           | 195          | 2621.7  | 952.2   | 973.9   | 1515.94              | 963.04                  | 781.97                  | 10.87                        |
| 3141.39    | 99           | 199          | 6275.0  | 1325    | 2575.0  | 3391.67              | 1950.00                 | 2101.72                 | 625.00                       |
| 3153.17    | 103          | 203          | 4827.6  | 1520.7  | 1382.8  | 2577.01              | 1451.72                 | 1592.39                 | 68.97                        |
| 3164.96    | 107          | 207          | 4312.5  | 1225.0  | 737.5   | 2091.67              | 981.25                  | 1582.93                 | 243.75                       |
| 3176.75    | 111          | 211          | 2508.3  | 1233.3  | 1488.9  | 1743.52              | 1361.11                 | 550.78                  | 127.78                       |
| 3188.53    | 115          | 215          | 4583.3  | 1316.7  | 1583.3  | 2494.44              | 1450.00                 | 1481.07                 | 133.33                       |
| 3200.32    | 119          | 219          | 4577.5  | 1172.5  | 1107.5  | 2285.83              | 1140.00                 | 1620.67                 | 32.50                        |
| 3212.11    | 123          | 223          | 5312.5  | 1187.5  | 1525.0  | 2675.00              | 1356.25                 | 1870.08                 | 168.75                       |
| 3223.89    | 127          | 227          | 3155.0  | 595.0   | 760.0   | 1503.33              | 677.50                  | 1169.85                 | 82.50                        |
| 3235.68    | 131          | 231          | 8422.2  | 988.9   | 1055.6  | 4705.56              | 1022.22                 | 3716.67                 | 33.33                        |
| 3247.47    | 135          | 235          | 2272.6  | 461.6   | 380.8   | 1367.12              | 421.23                  | 905.48                  | 40.41                        |
| 3259.25    | 139          | 239          | 2331.3  | 1650.0  | 656.3   | 1545.83              | 1153.13                 | 687.77                  | 496.88                       |
| 3271.04    | 143          | 243          | 657.5   | 90.0    | 352.5   | 366.67               | 221.25                  | 231.90                  | 131.25                       |
| 3282.83    | 147          | 247          | 1638.5  | 938.5   | 515.4   | 1030.77              | 726.92                  | 463.12                  | 211.54                       |
| 3294.61    | 151          | 251          | 1349.1  | 241.5   | 296.2   | 628.93               | 268.87                  | 509.70                  | 27.36                        |
| 3306.40    | 155          | 255          | 861.1   | 500.0   | 533.3   | 631.48               | 516.67                  | 162.94                  | 16.67                        |
| 3318.19    | 159          | 259          | 786.7   | 201.7   | 285.0   | 424.44               | 243.33                  | 258.38                  | 41.67                        |
| 3329.97    | 163          | 263          | 2000.0  | 686.7   | 766.7   | 1151.11              | 726.67                  | 601.14                  | 40.00                        |
| 3343.23    | 167.5        | 267.5        | 1413.1  | 203.3   | 360.7   | 659.02               | 281.97                  | 537.08                  | 78.69                        |
| 3353.55    | 171          | 271          | 775.0   | 741.7   | 516.7   | 677.78               | 629.17                  | 114.73                  | 112.50                       |
| 3366.81    | 175.5        | 275.5        | 1012.5  | 233.3   | 412.5   | 552.78               | 322.92                  | 333.20                  | 89.58                        |
| 3377.12    | 179          | 279          | 1500.0  | 440.0   | 570.0   | 836.67               | 505.00                  | 472.04                  | 65.00                        |
| 3388.91    | 183          | 283          | 1418.5  | 470.4   | 629.6   | 839.51               | 550.00                  | 414.55                  | 79.63                        |
| 3400.69    | 187          | 287          | 718.2   | 545.5   | 381.8   | 548.48               | 463.64                  | 137.34                  | 81.82                        |
| 3406.59    | 189          | 289          | 506.7   | 200.0   | 653.3   | 453.33               | 426.67                  | 188.88                  | 226.67                       |
|            |              |              |         |         |         |                      | Average SD              |                         |                              |
|            |              |              |         |         |         |                      | Total core              | 1673.60                 | 337.04                       |
|            |              |              |         |         |         |                      | Maivik                  | 2159.62                 | 483.92                       |
|            |              |              |         |         |         |                      | HUM3                    | 1326.43                 | 142.95                       |

## Appendix 2

### Geochemical data

These are the results from the ICP-MS and Elemental combustion system. All counts are expressed as ppb, with the exception of Carbon, Nitrogen and Sulphur which are expressed as percentages. Samples with 0 ppb, were below the detection limit of the ICP-MS of 5ppb. Sample depth is the actual sample number without correction for core shrinkage, actual depth is the depth in the core after correction for shrinkage using equation 3.1 outlined in section 3.1.1.

| Sample depth | Actual depth | Li         | Be        | B           | Na          | Al          | K            | Ca          | Ti          | V           | Cr         | Fe (54)     | Mn          | Fe (57)     |
|--------------|--------------|------------|-----------|-------------|-------------|-------------|--------------|-------------|-------------|-------------|------------|-------------|-------------|-------------|
| 0            | 0            | 10675.7082 | 0         | 6897.4163   | 921683.1905 | 19897821.72 | 3706874.838  | 6037558.664 | 1517989.54  | 862386.0836 | 8089.8049  | 16584547.39 | 160876.3984 | 13959734.13 |
| 2            | 2.65         | 2355.213   | 0         | 3112.503    | 852264.6265 | 13453516.63 | 2114722.587  | 4717127.5   | 1092846.697 | 725280.6768 | 5272.0959  | 1168564.87  | 87370.0501  | 9928852.556 |
| 4            | 5.29         | 5875.4881  | 0         | 13665.8429  | 792293.5753 | 15006714.33 | 2344325.384  | 4988692.558 | 1183265.272 | 827877.1363 | 5650.3736  | 14687578.23 | 104895.4456 | 12439998.4  |
| 6            | 7.94         | 8312.2666  | 0         | 853429.1599 | 15046531.78 | 2204492.57  | 113245.662   | 5232080.358 | 113245.662  | 772125.8339 | 7629.4021  | 16180639.69 | 90487.6156  | 13880998.3  |
| 8            | 10.59        | 9435.0303  | 0         | 5610.9367   | 791063.637  | 13633239.49 | 2085884.373  | 5086595.362 | 109448.736  | 613919.1871 | 5221.1222  | 12707983.91 | 85766.0814  | 10784097.78 |
| 10           | 13.24        | 4677.873   | 0         | 706076.4258 | 13658371.24 | 1999174.601 | 4804388.981  | 4804388.981 | 1069364.051 | 510277.971  | 5325.9342  | 13995812.53 | 84081.3175  | 11909195.02 |
| 12           | 15.88        | 8291.4397  | 0         | 1252.2798   | 764343.3634 | 14908879.39 | 2437001.215  | 5076591.911 | 1214817.969 | 554203.6875 | 5512.6762  | 15928666.44 | 107670.1981 | 13571575.31 |
| 14           | 18.53        | 1182.8446  | 0         | 11254.8576  | 669707.3708 | 14096933.69 | 1904208.201  | 5071306.231 | 1077652.829 | 333367.6742 | 5590.9483  | 18105827.74 | 13715174.44 | 15570471.19 |
| 16           | 21.18        | 5875.9518  | 0         | 825651.8299 | 14194582.66 | 2194480.608 | 4763881.164  | 1127194.955 | 314308.4276 | 0           | 5704.1815  | 14808483.77 | 99405.0874  | 12463826.3  |
| 18           | 23.82        | 2370.6795  | 2817.0076 | 3759.5312   | 935278.0745 | 13713388.42 | 2169282.011  | 4841197.257 | 1053051.997 | 110253.9923 | 5112.9665  | 15139233.71 | 97586.0829  | 12658058.36 |
| 20           | 26.47        | 3530.8651  | 0         | 0           | 796865.83   | 13908340.24 | 1999028.568  | 4875424.821 | 1087316.714 | 0           | 5221.0816  | 14973179.6  | 941883.729  | 12859739.42 |
| 22           | 29.12        | 5870.6239  | 0         | 6206.6016   | 935615.2143 | 15097623.49 | 2270373.953  | 5029457.666 | 1068896.892 | 0           | 6738.6314  | 15680408.28 | 110087.6644 | 13356636.25 |
| 24           | 31.76        | 5820.3374  | 0         | 801000.1485 | 14489049.14 | 2142732.152 | 4956543.45   | 1080729.398 | 105729.398  | 0           | 5413.9269  | 13688157.45 | 97496.3466  | 11596858.88 |
| 26           | 34.41        | 4744.3804  | 0         | 796865.83   | 13908340.24 | 1999028.568 | 4875424.821  | 1087316.714 | 105729.398  | 0           | 5148.5284  | 1511772.82  | 95283.1925  | 12940039.97 |
| 28           | 37.06        | 5900.3981  | 0         | 0           | 681456.2896 | 13882862.25 | 1978430.982  | 4734507.511 | 1015441.629 | 0.00        | 5283.1674  | 14017540.3  | 92609.8661  | 11999181.43 |
| 30           | 39.71        | 0.00       | 2794.98   | 0           | 839984.39   | 14551327.49 | 2341039.65   | 4958832.04  | 1099464.39  | 0           | 5457.47    | 14109401.84 | 100129.694  | 11989606.52 |
| 32           | 42.35        | 3533.5182  | 0         | 622.6236    | 588328.7961 | 14217794.56 | 2059672.551  | 4731759.216 | 1125495.363 | 0           | 5128.7373  | 14151795.74 | 94961.1094  | 12193567.15 |
| 34           | 45           | 3530.4466  | 0         | 0           | 724075.4526 | 14013608.52 | 2071853.016  | 4645118.546 | 1135897.912 | 0           | 5033.4389  | 13346392.12 | 92426.7453  | 11497415.01 |
| 36           | 47.65        | 7066.1988  | 0         | 0           | 724030.4925 | 13730779.02 | 1998029.698  | 4460659.548 | 1096791.153 | 0           | 5315.2934  | 13129273.48 | 87700.5935  | 11319118.03 |
| 38           | 50.29        | 2348.4345  | 0         | 0           | 542158.4425 | 13864941.75 | 1889471.465  | 4525615.5   | 1063607.009 | 0           | 5000.9989  | 14502557.33 | 92760.5316  | 12719832.7  |
| 40           | 52.94        | 5812.1108  | 0         | 0           | 620097.2536 | 16244625.57 | 2824309.151  | 5249129.011 | 1428833.919 | 0           | 5846.6642  | 14228948.17 | 137347.552  | 12493158.71 |
| 42           | 55.59        | 5938.7536  | 0         | 0           | 535986.4778 | 14596592.97 | 2202310.929  | 4590904.285 | 1228259.026 | 0           | 5522.4524  | 12775550.47 | 106734.1296 | 10801908.21 |
| 44           | 58.24        | 0          | 0         | 0           | 0           | 0           | 0            | 0           | 0           | 0           | 150.6988   | 8036.0124   | 0           | 0           |
| 46           | 60.88        | 8276.9557  | 0         | 0           | 746641.1321 | 15336324.18 | 2270701.282  | 4812532.228 | 1226747.809 | 0           | 5229.2268  | 13525338.29 | 98356.8271  | 11659790.52 |
| 48           | 63.53        | 3558.0018  | 0         | 0           | 630638.5078 | 15441350.92 | 2354319.531  | 4450041.841 | 1210771.774 | 0           | 5622.0211  | 13544926.97 | 103849.4679 | 11675867.98 |
| 50           | 66.18        | 3538.5561  | 0         | 0           | 715381.7672 | 15545370.02 | 2427702.252  | 4512094.865 | 1132024.32  | 0           | 5650.2091  | 13178483.77 | 101102.9419 | 10896878.49 |
| 52           | 68.82        | 24834.8231 | 0         | 2500.5817   | 1095769.85  | 22916400.55 | 4073803.079  | 5923547.708 | 1038349.579 | 0           | 8215.7531  | 18198966.96 | 158361.2262 | 10703340.16 |
| 54           | 71.47        | 43662.9945 | 0         | 39923.7857  | 819557.1788 | 1927602.70  | 2149466.654  | 5429036.381 | 1002379.119 | 3683591.224 | 5920.8157  | 12790543.3  | 108183.1278 | 9685327.333 |
| 56           | 74.12        | 11142.4821 | 2345.3521 | 11472.2307  | 567746.1513 | 14050683.41 | 3139850.709  | 11356951.24 | 1745001.08  | 0           | 10008.2763 | 10011669.87 | 99984.0497  | 11889029.32 |
| 58           | 76.76        | 6653.1507  | 521.313   | 45342.0311  | 560196.8025 | 12046777.57 | 2406288.085  | 12279221.41 | 147252.056  | 0           | 8856.5142  | 8719183.62  | 79052.2435  | 10395272.19 |
| 60           | 79.41        | 5837.4965  | 262.088   | 29189.2739  | 621674.862  | 12721984.05 | 2459286.053  | 13962956.89 | 1472223.485 | 0           | 9674.6013  | 9685396.533 | 81067.7261  | 12068149.76 |
| 62           | 82.06        | 6051.2508  | 260.2856  | 16702.8648  | 581888.5628 | 13073603.26 | 2731085.949  | 14358318.87 | 1569928.513 | 0           | 8593.3708  | 9872452.474 | 93902.2584  | 12785178.06 |
| 64           | 84.71        | 4407.872   | 1303.489  | 11060.687   | 571575.684  | 13532659.4  | 2834693.452  | 25439441.28 | 1808484.181 | 0           | 12295.81   | 9875348.337 | 90071.088   | 14436610.71 |
| 66           | 87.35        | 5051.425   | 522.202   | 13154.882   | 588718.44   | 14246629.85 | 3136628.97   | 30772499.44 | 1996345.632 | 0           | 11573.396  | 8423651.815 | 104352.598  | 11921637.89 |
| 67           | 88.68        | 5441.665   | 261.495   | 12758.686   | 637181.622  | 14342908.02 | 3410488.311  | 28267243.41 | 2001664.408 | 0           | 11351.735  | 9069448.885 | 108591.948  | 13555470.68 |
| 68           | 90           | 0          | 0         | 0           | 0           | 0           | 0            | 0           | 0           | 0           | 0          | 0           | 0           | 0           |
| 100          | 100          | 4766.123   | 666.277   | 29881.734   | 909201.969  | 12631097.12 | 3164398.689  | 72361883.31 | 1530979.07  | 0           | 17604.133  | 15029366.9  | 82102.71    | 19064481.92 |
| 103          | 103          | 5537.451   | 655.012   | 34737.942   | 1398992.427 | 13331777.63 | 3987014.533  | 7739409.61  | 1760753.561 | 0           | 20112.136  | 9593050.59  | 91114.341   | 9094281.826 |
| 107          | 107          | 6893.242   | 0         | 17775.253   | 1082105.279 | 18018047.04 | 3580082.168  | 18799553.67 | 2118287.668 | 50522.718   | 13702.25   | 18370597.09 | 129781.933  | 21871566.68 |
| 111          | 111          | 6724.862   | 520.304   | 18901.807   | 754974.915  | 1711848.09  | 4741550.887  | 29861729.39 | 2788419.781 | 0           | 13196.615  | 12207697.29 | 143726.409  | 19298937.89 |
| 115          | 115          | 4518.395   | 661.725   | 28777.044   | 1088431.98  | 14757152.33 | 3684731.572  | 77992775.02 | 1893498.199 | 0           | 19936.099  | 12838090.35 | 95900.718   | 14810564.36 |
| 119          | 119          | 5212.279   | 654.296   | 21860.957   | 945049.246  | 16031547.21 | 4030428.595  | 80958215.82 | 2051042.636 | 0           | 18578.639  | 13674112.25 | 114403.524  | 1660578.36  |
| 123          | 123          | 6280.38    | 1309.502  | 24306.863   | 737095.999  | 17059604.35 | 3730799.29   | 8103326.22  | 2070970.27  | 0           | 19883.554  | 1113248.75  | 103764.218  | 11543182.97 |
| 127          | 127          | 5080.43    | 787.8     | 13369.687   | 825377.956  | 17151952.02 | 4253988.473  | 33467537.18 | 2249707.451 | 0           | 14097.772  | 9785059.956 | 120365.819  | 14815821.87 |
| 131          | 131          | 12170.87   | 1047.019  | 21517.02    | 822709.233  | 22739148.42 | 69997827.909 | 35429780.64 | 3866248.432 | 0           | 16339.284  | 16265353.36 | 253440.159  | 27667643.73 |
| 135          | 135          | 6783.008   | 1312.007  | 21152.686   | 851141.32   | 18958766.33 | 5215473.72   | 35441214.16 | 2786110.125 | 0           | 14346.319  | 11326976.16 | 155635.3    | 17688902.09 |
| 139          | 139          | 645.225    | 1322.918  | 0           | 0           | 0           | 0            | 0           | 0           | 626597.427  | 46351.662  | 51195714.55 | 220726.429  | 0           |
| 143          | 143          | 4733.225   | 1049.146  | 26985.72    | 544393.551  | 15681369.03 | 3560786.43   | 39377814.61 | 1985112.23  | 0           | 13835.084  | 10163633.55 | 112558.524  | 15942481.73 |
| 147          | 147          | 2111.306   | 0         | 0           | 0           | 218711.053  | 6105089.594  | 1361339399  | 0           | 1343986.246 | 100566.558 | 106162579.2 | 448096.223  | 0           |
| 151          | 151          | 3099.598   | 657.431   | 43582.856   | 1139696.556 | 13861534.52 | 3538925.101  | 96715030.81 | 1553418.683 | 0           | 22274.727  | 9175323.394 | 80093.063   | 8376887.06  |
| 154          | 154          | 24170.501  | 4261.367  | 207040.067  | 2453949.452 | 15227815.28 | 2540564.662  | 37549125.99 | 1423921.008 | 54586.541   | 13673.582  | 1068424.96  | 96850.458   | 12427958.72 |

| Sample depth | Actual depth | Li        | Be         | B          | Na          | Al          | K           | Ca          | Ti         | V           | Cr          | Fe (54)    | Mn          | Fe (57) |
|--------------|--------------|-----------|------------|------------|-------------|-------------|-------------|-------------|------------|-------------|-------------|------------|-------------|---------|
| 155          | 15257.353    | 0         | 117524.988 | 1546214.76 | 14543115.28 | 2311652.327 | 31771077.53 | 1377365.11  | 34065.538  | 10995.625   | 10571152.02 | 86606.274  | 12558977.53 |         |
| 159          | 14224.09     | 1925.698  | 127274.602 | 831894.17  | 18303543.84 | 4893338.75  | 10776538.51 | 2469755.314 | 82602.733  | 12251.748   | 15861254.59 | 218881.554 | 18814285.81 |         |
| 163          | 9722.914     | 0         | 78503.977  | 1524701.78 | 13040884.2  | 2282521.562 | 32888912.16 | 1431498.689 | 51335.644  | 12392.524   | 11908603.31 | 82591.277  | 13630609.19 |         |
| 167          | 4661.727     | 0         | 13732.713  | 641966.982 | 11689537.16 | 2263973.028 | 9644497.121 | 1338951.788 | 37805.1    | 7643.519    | 12347503.86 | 78692.64   | 15188616.45 |         |
| 171          | 6305.078     | 358.02    | 17293.83   | 799174.395 | 13886750.83 | 2775973.438 | 7471466.109 | 1482786.073 | 36516.625  | 9435.765    | 13466382.04 | 103597.929 | 16046613.27 |         |
| 175          | 11993.918    | 1503.324  | 20265.182  | 960440.717 | 20338066.2  | 6475448.05  | 9380170.643 | 3409773.251 | 82930.161  | 13287.458   | 17685029.26 | 266537.195 | 21333198.43 |         |
| 179          | 8255.278     | 712.768   | 14612.556  | 680008.99  | 14764874.48 | 3145763.432 | 7298848.127 | 1793240.296 | 37490.085  | 10147.622   | 15877306.29 | 128506.167 | 19213872.81 |         |
| 183          | 1246.169     | 0         | 0          | 0          | 1641.885    | 1310038.5   | 1071750098  | 0           | 979899.767 | 32166.862   | 38123052.68 | 122797.212 | 0           |         |
| 187          | 1608.432     | 533.569   | 0          | 0          | 1601038.439 | 1689255422  | 0           | 510707.086  | 50733.069  | 65398471.13 | 201221.568  | 0          | 0           |         |
| 195          | 442.211      | 0         | 9754.332   | 0          | 528701.362  | 698140690.3 | 0           | 368955.696  | 20118.614  | 28869676.23 | 84709.798   | 0          | 0           |         |
| 199          | 0            | 180974.41 | 0          | 0          | 183970.424  | 19957143190 | 0           | 982286.035  | 38583.478  | 77130181.22 | 248108.107  | 0          | 0           |         |
| 203          | 169.124      | 1065.975  | 222730.482 | 0          | 245909.17   | 4188109640  | 0           | 2084170.765 | 68144.831  | 146173731.3 | 524634.972  | 0          | 0           |         |
| 207          | 68.22        | 214.992   | 17871.906  | 0          | 33600.225   | 868858635.5 | 0           | 433830.441  | 13676.881  | 29185472.06 | 111404.834  | 0          | 0           |         |
| 211          | 282.978      | 0         | 19635.079  | 0          | 26033.495   | 1488724896  | 0           | 749588.033  | 21003.427  | 48507094.28 | 190805.329  | 0          | 0           |         |
| 215          | 34.08        | 429.607   | 8928.082   | 0          | 0           | 906643846.4 | 0           | 459109.314  | 14936.382  | 29023549.13 | 116454.016  | 0          | 0           |         |
| 219          | 226.606      | 714.139   | 8423.393   | 0          | 0           | 157117864   | 0           | 775682.567  | 21447.059  | 46828747.68 | 201310.769  | 0          | 0           |         |
| 223          | 0            | 0         | 0          | 0          | 0           | 1113.735    | 1339628483  | 0           | 673064.973 | 10750.202   | 11873596.35 | 167531.697 | 0           | 0       |
| 227          | 0            | 0         | 9667.79    | 0          | 0           | 2418635374  | 0           | 1198958.421 | 34218.179  | 69604519.75 | 308271.128  | 0          | 0           |         |
| 231          | 68.127       | 0         | 0          | 0          | 0           | 997467521.6 | 0           | 508453.935  | 12320.544  | 26390793.19 | 130046.941  | 0          | 0           |         |
| 235          | 0            | 0         | 0          | 0          | 0           | 1056273997  | 0           | 536653.625  | 13239.044  | 23601149.71 | 141176.562  | 0          | 0           |         |
| 239          | 0            | 643.665   | 0          | 0          | 0           | 1111898486  | 0           | 561728.029  | 11603.652  | 22087661.22 | 145351.101  | 0          | 0           |         |
| 243          | 0            | 0         | 0          | 0          | 0           | 1204226237  | 0           | 603638.866  | 12053.558  | 20422156.96 | 153157.406  | 0          | 0           |         |
| 247          | 34.109       | 0         | 0          | 0          | 0           | 1213287547  | 0           | 605702.456  | 11975.112  | 20173811.68 | 153593.387  | 0          | 0           |         |
| 251          | 0            | 1059.26   | 0          | 0          | 0           | 6053219952  | 0           | 3018887.51  | 61313.405  | 96114042.24 | 759466.542  | 0          | 0           |         |
| 255          | 255          | 214.461   | 0          | 0          | 0           | 1245979394  | 0           | 629774.02   | 11919.273  | 19268210.87 | 158690.176  | 0          | 0           |         |
| 259          | 68.171       | 214.838   | 0          | 0          | 0           | 5822.746    | 1290787314  | 654151.629  | 12261.483  | 17291366.11 | 167045.468  | 0          | 0           |         |
| 263          | 0            | 0         | 0          | 0          | 0           | 3620.557    | 1306806291  | 664989.194  | 11660.03   | 15431354.07 | 168184.849  | 0          | 0           |         |
| 267.5        | 267.5        | 0         | 0          | 0          | 0           | 22821.216   | 1339609042  | 680399.831  | 11135.701  | 16159444.76 | 173328.2    | 0          | 0           |         |
| 271          | 271          | 0         | 0          | 0          | 0           | 71303.539   | 1439232794  | 732411.338  | 11275.067  | 12282953.13 | 183940.122  | 0          | 0           |         |
| 275.5        | 275.5        | 0         | 0          | 0          | 0           | 27322.617   | 3363603356  | 1700750.467 | 26369.207  | 29276096.7  | 424007.274  | 0          | 0           |         |
| 279          | 279          | 0         | 0          | 0          | 0           | 69924.91    | 1420341886  | 7255684.595 | 10004.604  | 12286985.74 | 180778.77   | 0          | 0           |         |
| 283          | 283          | 0         | 0          | 0          | 0           | 218553.515  | 3636461103  | 1854438.075 | 30833.118  | 31114708.5  | 472148.345  | 0          | 0           |         |
| 287          | 287          | 0         | 214.452    | 0          | 0           | 49375.715   | 1404302700  | 712828.241  | 12012.334  | 12063081.11 | 177447.035  | 0          | 0           |         |
| 289          | 289          | 0         | 214.683    | 0          | 0           | 41270.143   | 1385587748  | 703464.08   | 10500.336  | 11975254.53 | 176035.034  | 0          | 0           |         |

| Sample depth | Actual depth | Ni         | Co         | Cu          | Zn          | As        | Se          | Sr         | Mo         | Ag (Calibration wrong) | Cd        | Sb        | Ba         |
|--------------|--------------|------------|------------|-------------|-------------|-----------|-------------|------------|------------|------------------------|-----------|-----------|------------|
| 0            | 0            | 0          | 5418.7978  | 2817.173367 | 1493923.258 | 7631.8201 | 131974.1064 | 35394.363  | 15466.1333 | 30630.7206             | 2143.7183 | 680.715   | 56445.3203 |
| 2            | 2.65         | 23347.3482 | 4022.455   | 208223.5392 | 1068538.881 | 782.9803  | 103369.9217 | 27783.9715 | 10045.2755 | 23057.366              | 1284.6787 | 337.8945  | 35253.3887 |
| 4            | 5.29         | 0          | 4589.3634  | 226020.3099 | 1165895.924 | 8799.8803 | 110614.1657 | 31559.8011 | 15258.8816 | 35096.0804             | 1100.2539 | 291.1962  | 38738.0882 |
| 6            | 7.94         | 0          | 4834.6167  | 225206.886  | 1098555.906 | 8892.5089 | 89424.4578  | 30501.9969 | 12547.1952 | 31421.8731             | 1495.0534 | 309.7487  | 41212.3833 |
| 8            | 10.59        | 20259.0936 | 4626.7041  | 210815.1878 | 1073847.612 | 7961.1809 | 103832.8481 | 31875.0407 | 14111.9772 | 36144.2945             | 1770.6444 | 215.3473  | 35562.7133 |
| 10           | 13.24        | 0          | 4765.3742  | 210339.1822 | 1034913.853 | 8942.7476 | 102950.8667 | 31287.3572 | 8251.4058  | 26465.5035             | 1384.2278 | 305.0539  | 34428.1557 |
| 12           | 15.88        | 0          | 5803.4001  | 230755.5969 | 1170651.946 | 8245.5595 | 115563.0859 | 32472.446  | 14745.442  | 29158.3402             | 1230.9326 | 355.3186  | 39325.9686 |
| 14           | 18.53        | 0          | 10774.8822 | 200766.8807 | 1028972.149 | 8234.0977 | 110411.2386 | 26917.6938 | 12316.5424 | 33984.8313             | 933.6806  | 200.553   | 30533.7119 |
| 16           | 21.18        | 0          | 5230.6812  | 218432.8118 | 1101120.145 | 6383.5088 | 120591.7257 | 31989.6826 | 9995.1623  | 33074.5665             | 1343.8794 | 153.2732  | 36401.4199 |
| 18           | 23.82        | 0          | 5353.5657  | 209126.5536 | 1036824.516 | 7751.3754 | 113458.8375 | 31225.7185 | 6433.3393  | 33704.5665             | 1384.1393 | 371.0328  | 37123.7292 |
| 20           | 26.47        | 0          | 5173.559   | 212019.6467 | 1006034.005 | 6827.5765 | 112977.8072 | 32534.6783 | 12613.4043 | 36404.0073             | 1631.634  | 245.6054  | 35487.9077 |
| 22           | 29.12        | 0          | 5347.4774  | 198249.1569 | 1079728.25  | 8173.3954 | 114869.8365 | 32775.798  | 12734.0738 | 35816.6878             | 1209.7888 | 214.3879  | 41210.0419 |
| 24           | 31.76        | 0          | 4947.4306  | 208902.6377 | 1033436.978 | 9054.3853 | 132156.6706 | 32532.0001 | 10130.1129 | 36876.0011             | 1126.7479 | 138.9879  | 36664.2771 |
| 26           | 34.41        | 0          | 5496.1258  | 199790.455  | 1007377.789 | 6067.4339 | 114458.5257 | 31819.5171 | 10389.8286 | 36602.5695             | 1191.9769 | 139.2259  | 34575.0888 |
| 28           | 37.06        | 0          | 5175.0778  | 194281.856  | 976344.1546 | 8650.4865 | 131396.9555 | 32287.6811 | 10729.0481 | 38007.5815             | 1539.8045 | 230.8663  | 35829.9604 |
| 30           | 39.71        | 0.00       | 6890.30    | 213497.03   | 1046294.69  | 6760.43   | 144315.59   | 32084.35   | 8028.65    | 52896.75               | 1196.96   | 230.08    | 39950.48   |
| 32           | 42.35        | 0          | 5388.7806  | 210110.4466 | 1054710.723 | 7578.0961 | 142961.0599 | 32518.4154 | 10915.6579 | 49550.2661             | 1035.8274 | 168.9806  | 36385.5393 |
| 34           | 45           | 0          | 5660.2171  | 215015.1303 | 1070999.315 | 8254.1887 | 156882.1546 | 31524.5957 | 9348.1429  | 51009.9725             | 1282.8953 | 291.6219  | 36180.5432 |
| 36           | 47.65        | 0          | 5672.597   | 207699.0829 | 1015785.163 | 7577.1971 | 151335.3179 | 31231.5055 | 10345.3559 | 60071.791              | 1711.4421 | 276.4809  | 35400.4595 |
| 38           | 50.29        | 0          | 6372.9695  | 212208.5614 | 984016.8455 | 7678.6414 | 156212.771  | 32713.0937 | 13092.4339 | 68724.4324             | 1445.4442 | 214.4048  | 34221.904  |
| 40           | 52.94        | 0          | 6874.4631  | 242014.4225 | 1300449.838 | 7420.5081 | 214884.1347 | 36572.12   | 16196.0846 | 78516.1162             | 2310.5807 | 215.903   | 46472.9808 |
| 42           | 55.59        | 14115.1222 | 6376.748   | 222163.9415 | 1135290.946 | 7892.478  | 200062.4472 | 32565.3716 | 10798.7902 | 84331.485              | 2111.1924 | 278.8405  | 37140.3349 |
| 44           | 58.24        | 1487.7519  | 4593.0134  | 0           | 0           | 0         | 11285.8524  | 0          | 0          | 840.9235               | 0         | 15.4603   | 0          |
| 46           | 60.88        | 0          | 8930.8399  | 230416.3977 | 1136925.472 | 8978.4462 | 258061.0322 | 35290.8316 | 16496.5711 | 142523.9787            | 1868.5584 | 323.8545  | 38427.5349 |
| 48           | 63.53        | 0          | 8605.9118  | 221243.6726 | 1094849.146 | 7568.0582 | 21660.7255  | 33752.5055 | 12025.5605 | 196136.6808            | 7928.803  | 340.303   | 39247.9254 |
| 50           | 66.18        | 17908.3977 | 10052.6386 | 220369.1328 | 1088883.761 | 7982.1288 | 277342.0302 | 33614.1234 | 11145.7805 | 217326.3877            | 1558.406  | 246.1404  | 40900.1712 |
| 52           | 68.82        | 0          | 10871.6336 | 309394.8682 | 1582434.303 | 5114.0968 | 325860.4235 | 44070.8859 | 27707.5745 | 110411.3195            | 1678.5371 | 323.906   | 56102.9675 |
| 54           | 71.47        | 0          | 8738.0466  | 23120.3865  | 899096.3501 | 7343.5731 | 53162.2638  | 32931.3874 | 31872.2988 | 13729.4716             | 1313.1199 | 200.0841  | 31169.9289 |
| 56           | 74.12        | 12590.2448 | 0          | 10018.7919  | 370081.7501 | 6724.0353 | 8437.868    | 31765.311  | 26297.8954 | 33305.8472             | 2279.6888 | 1413.1593 | 45705.5243 |
| 58           | 76.76        | 12223.4912 | 0          | 9232.9756   | 315510.8291 | 4483.7529 | 8.8178      | 28357.6481 | 7509.5913  | 25803.6839             | 1765.748  | 471.1642  | 35367.0044 |
| 60           | 79.41        | 9820.9487  | 0          | 273579.8886 | 5635.4738   | 0         | 29053.1702  | 5043.1951  | 0          | 28849.7513             | 1407.4231 | 473.7519  | 36388.0725 |
| 62           | 82.06        | 13488.2186 | 0          | 289839.2648 | 12499.352   | 2283.8228 | 2283.8228   | 29440.6633 | 3972.2422  | 62494.9313             | 1273.6863 | 256.6329  | 37824.4772 |
| 64           | 84.71        | 14810.709  | 0          | 3040.572    | 277232.882  | 10463.758 | 0           | 29020.392  | 2139.934   | 24844.789              | 964.355   | 0         | 39749.785  |
| 66           | 87.35        | 6061.792   | 0          | 0           | 271041.823  | 9357.086  | 7414.754    | 33616.638  | 1471.313   | 14852.739              | 1128.782  | 0         | 42257.255  |
| 67           | 88.68        | 10404.831  | 0          | 0           | 282347.828  | 8808.931  | 7999.55     | 33667.362  | 1508.928   | 16613.81               | 1299.93   | 0         | 44802.286  |
| 68           | 90           | 0          | 0          | 0           | 0           | 0         | 0           | 0          | 0          | 0                      | 0         | 0         | 0          |
| 100          | 100          | 689.145    | 0          | 244691.024  | 9550.958    | 0         | 21602.241   | 1432.326   | 0          | 32978.983              | 315.098   | 0         | 36587.514  |
| 103          | 103          | 0          | 0          | 398997.188  | 5633.677    | 0         | 144.03      | 32740.797  | 2605.2     | 40647.689              | 1358.029  | 0         | 49851.306  |
| 107          | 107          | 29415.026  | 1554.99    | 832.162     | 42424.626   | 14882.435 | 31756.058   | 35342.712  | 4485.448   | 34641.635              | 2492.311  | 0         | 66376.492  |
| 111          | 111          | 16811.833  | 0          | 7810.342    | 411029.761  | 10068.926 | 0           | 38199.325  | 945.271    | 24216.193              | 1680.308  | 21.375    | 63231.175  |
| 115          | 115          | 3300.414   | 0          | 0           | 312727.606  | 16599.98  | 8798.79     | 28589.154  | 1120.521   | 37642.262              | 1288.81   | 0         | 47706.279  |
| 119          | 119          | 3404.577   | 0          | 0           | 262234.858  | 8548.162  | 0           | 30695.861  | 27552.19   | 27552.19               | 189.596   | 53.759    | 50306.193  |
| 123          | 123          | 0          | 0          | 0           | 246644.374  | 6570.009  | 0           | 33017.177  | 1601.595   | 28538.784              | 268.732   | 0         | 61910.037  |
| 127          | 127          | 17340.963  | 0          | 19681.675   | 421841.449  | 6399.351  | 620.45      | 37067.386  | 1185.061   | 22116.065              | 975.966   | 0         | 62032.004  |
| 131          | 131          | 0          | 0          | 0           | 468925.235  | 5628.306  | 7954.376    | 44357.267  | 885.425    | 14309.803              | 490.428   | 129.041   | 91806.43   |
| 135          | 135          | 17289.745  | 0          | 0           | 341716.566  | 6582.58   | 6871.651    | 39986.36   | 914.577    | 11631.2                | 436.162   | 21.56     | 65962.637  |
| 139          | 139          | 12890.924  | 0          | 0           | 8748.545    | 474.094   | 149581.789  | 8523.697   | 0          | 13193.908              | 17.284    | 597.828   | 0          |
| 143          | 143          | 0          | 0          | 0           | 317423.046  | 5263.755  | 0           | 36430.319  | 1106.676   | 14338.869              | 1533.499  | 0         | 44888.094  |
| 147          | 147          | 0          | 0          | 0           | 0           | 0         | 0           | 0          | 0          | 0                      | 0         | 0         | 0          |
| 151          | 151          | 54936.243  | 0          | 0           | 225656.484  | 3298.449  | 387093.526  | 36723.521  | 1307.453   | 35497.916              | 583.915   | 533.513   | 34441.7    |
| 154          | 154          | 5668.506   | 1593.234   | 0           | 282498.074  | 2162.823  | 0           | 36245.05   | 40066.673  | 165476.656             | 4910.018  | 3339.161  | 42780.858  |

| Sample depth | Actual depth | Ni        | Co         | Cu        | Zn         | As        | Se         | Sr        | Mo        | Ag (Calibration wrong) | Cd       | Sb       | Ba        |
|--------------|--------------|-----------|------------|-----------|------------|-----------|------------|-----------|-----------|------------------------|----------|----------|-----------|
| 155          | 155          | 10471.573 | 948.243    | 41301.705 | 327302.081 | 5721.09   | 0          | 31343.5   | 20002.783 | 94766.705              | 2497.024 | 401.487  | 36415.707 |
| 159          | 159          | 0         | 3293.504   | 0         | 551593.466 | 12597.283 | 21284.716  | 39420.463 | 25601.853 | 32010.375              | 4656.078 | 2702.92  | 65685.337 |
| 163          | 163          | 6701.181  | 2894.185   | 0         | 346928.741 | 10185.942 | 29129.993  | 27850.38  | 14082.498 | 791073.812             | 1514.353 | 919.049  | 38121.909 |
| 167          | 167          | 25391.898 | 2156.404   | 36681.205 | 27847.258  | 6821.423  | 17315.405  | 26217.717 | 3269.997  | 25072.357              | 1570.85  | 244.445  | 35730.087 |
| 171          | 171          | 22511.425 | 2224.086   | 12219.811 | 421096.342 | 4603.328  | 29866.838  | 28281.379 | 4074.357  | 41561.301              | 2476.795 | 306.044  | 41881.58  |
| 175          | 175          | 0         | 2144.506   | 40553.317 | 544133.491 | 4650.673  | 18506.273  | 45023.578 | 2162.224  | 22472.831              | 1174.981 | 0        | 82440.787 |
| 179          | 179          | 31733.366 | 1812.133   | 0         | 301560.453 | 5788.159  | 13432.894  | 29570.036 | 3281.754  | 14567.338              | 868.268  | 0        | 45233.369 |
| 183          | 183          | 5402.3    | 17243.132  | 0         | 14838.667  | 0         | 113952.302 | 0         | 6129.236  | 0                      | 578.147  | 0        | 0         |
| 187          | 187          | 4688.899  | 30779.334  | 0         | 35571.553  | 722.156   | 197333.608 | 0         | 10904.91  | 0                      | 1367.801 | 0        | 0         |
| 195          | 195          | 2120.443  | 16630.816  | 0         | 15720.863  | 0         | 89534.806  | 0         | 4357.139  | 0                      | 545.776  | 122.183  | 0         |
| 199          | 199          | 2459.951  | 69071.209  | 0         | 65958.849  | 0         | 215060.656 | 0         | 13563.785 | 0                      | 810.553  | 152.505  | 0         |
| 203          | 203          | 6215.766  | 84526.131  | 0         | 138291.469 | 0         | 560305.615 | 0         | 27886.161 | 0                      | 1287.621 | 303.74   | 0         |
| 207          | 207          | 1212.784  | 14984.577  | 0         | 30434.264  | 0         | 131460.559 | 0         | 6327.282  | 0                      | 330.162  | 81.68    | 0         |
| 211          | 211          | 1811.69   | 34779.252  | 0         | 57482.135  | 0         | 245213.117 | 0         | 9623.36   | 0                      | 474.422  | 304.928  | 0         |
| 215          | 215          | 1047.332  | 23830.219  | 0         | 30430.682  | 0         | 93724.078  | 0         | 4565.689  | 0                      | 371.862  | 61.206   | 0         |
| 219          | 219          | 1675.823  | 45563.311  | 0         | 49066.803  | 0         | 210587.314 | 0         | 6713.864  | 0                      | 658.712  | 339.146  | 0         |
| 223          | 223          | 0         | 19347.539  | 0         | 27124.651  | 0         | 238944.311 | 0         | 10350.697 | 0                      | 1160.312 | 264.974  | 0         |
| 227          | 227          | 2524.251  | 88991.14   | 0         | 81163.98   | 0         | 399829.964 | 0         | 16709.679 | 0                      | 937.227  | 766.334  | 0         |
| 231          | 231          | 1005.138  | 48639.237  | 0         | 32545.436  | 871.757   | 151437.801 | 0         | 8424.934  | 0                      | 714.251  | 142.746  | 0         |
| 235          | 235          | 1019.583  | 48052.071  | 0         | 30781.478  | 0         | 182398.235 | 0         | 7384.19   | 0                      | 651.948  | 347.252  | 0         |
| 239          | 239          | 0         | 55201.286  | 0         | 31300.039  | 1451.943  | 188663.283 | 0         | 8770.025  | 0                      | 729.305  | 387.192  | 0         |
| 243          | 243          | 191.361   | 19211.032  | 0         | 31288.449  | 0         | 163395.207 | 0         | 8961.863  | 0                      | 895.418  | 81.664   | 0         |
| 247          | 247          | 36.354    | 18110.782  | 0         | 30486.675  | 436.453   | 192132.76  | 0         | 10017.803 | 0                      | 774.437  | 163.354  | 0         |
| 251          | 251          | 0         | 95694.933  | 0         | 154440.187 | 0         | 840181.403 | 0         | 46761.505 | 0                      | 2522.716 | 1870.962 | 0         |
| 255          | 255          | 296.105   | 25702.47   | 0         | 31447.321  | 870.784   | 202513.26  | 0         | 10168.772 | 0                      | 771.457  | 427.762  | 0         |
| 259          | 259          | 0         | 38402.398  | 0         | 34320.959  | 1017.699  | 166819.883 | 0         | 8957.212  | 0                      | 696.233  | 530.54   | 0         |
| 263          | 263          | 0         | 43287.377  | 0         | 29992.911  | 2617.151  | 211042.542 | 0         | 10011.803 | 0                      | 805.411  | 571.397  | 0         |
| 267.5        | 267.5        | 0         | 21766.481  | 0         | 30422.193  | 2180.524  | 222875.861 | 0         | 13544.736 | 0                      | 977.73   | 285.641  | 0         |
| 271          | 271          | 0         | 108281.257 | 0         | 28673.205  | 1019.286  | 177376.555 | 0         | 13544.736 | 0                      | 778.422  | 408.744  | 0         |
| 275.5        | 275.5        | 0         | 46774.758  | 0         | 70877.841  | 723.232   | 597691.004 | 0         | 34947.76  | 0                      | 1477.444 | 1015.082 | 0         |
| 279          | 279          | 0         | 23197.426  | 0         | 29224.972  | 726.348   | 203144.263 | 0         | 13337.364 | 0                      | 939.499  | 305.837  | 0         |
| 283          | 283          | 0         | 60923.582  | 0         | 72650.343  | 16744.103 | 536315.38  | 0         | 33419.402 | 0                      | 2100.179 | 868.512  | 0         |
| 287          | 287          | 0         | 21738.035  | 0         | 29395.98   | 1306.124  | 236986.642 | 0         | 12272.172 | 0                      | 1019.112 | 264.794  | 0         |
| 289          | 289          | 0         | 20279.187  | 0         | 28449.068  | 1452.812  | 193175.837 | 0         | 11407.862 | 0                      | 938.475  | 468.987  | 0         |

| Sample depth | Actual depth | Ti        | Pb 206    | Pb 207     | Pb 208    | Bi      | N(%)        | C(%)        | S(%)        |
|--------------|--------------|-----------|-----------|------------|-----------|---------|-------------|-------------|-------------|
| 0            | 0            | 425.6674  | 6217.9252 | 14901.0464 | 6200.4349 | 66.8981 | 2.65075     | 38.09885    | 0.71885     |
| 2            | 2.65         | 246.9957  | 4837.5105 | 11149.5644 | 4568.4244 | 61.9884 | 3.03245     | 38.792075   | 0.9129      |
| 4            | 5.29         | 260.4868  | 4483.5878 | 10884.1859 | 4515.339  | 0       | 3.1392      | 44.4055     | 0.91105     |
| 6            | 7.94         | 249.0638  | 5394.6327 | 12452.1296 | 5293.2325 | 0       | 3.18435     | 41.9165     | 0           |
| 8            | 10.59        | 207.507   | 3999.4468 | 8752.87    | 4021.8523 | 0       | 3.122383333 | 40.986625   | 1.0316      |
| 10           | 13.24        | 216.2259  | 3761.4942 | 9263.3007  | 3713.6757 | 0       | 3.1861      | 39.613075   | 0           |
| 12           | 15.88        | 196.6321  | 4312.4575 | 9150.3427  | 4059.1376 | 0       | 2.92875     | 38.261      | 1.164166667 |
| 14           | 18.53        | 196.3588  | 4234.7564 | 9230.276   | 3851.3023 | 0       | 3.05125     | 38.675125   | 1.1485      |
| 16           | 21.18        | 165.8831  | 4002.0066 | 9400.6781  | 4202.547  | 0       | 3.17075     | 43.77175    | 1.12775     |
| 18           | 23.82        | 200.3078  | 4294.4122 | 9713.9878  | 4379.8829 | 0       | 3.16885     | 41.20165    | 0           |
| 20           | 26.47        | 184.8515  | 4755.0898 | 11443.0219 | 4832.1536 | 0       | 3.1233      | 44.5742     | 1.20695     |
| 22           | 29.12        | 166.8999  | 5522.4373 | 13312.4167 | 5442.3439 | 0       | 3.00715     | 38.03995    | 0           |
| 24           | 31.76        | 176.5524  | 4910.498  | 11349.8602 | 4910.3643 | 0       | 3.2205      | 44.10795    | 1.02915     |
| 26           | 34.41        | 165.0643  | 4136.423  | 9964.0603  | 3979.1613 | 0       | 3.1611      | 43.61025    | 1.23435     |
| 28           | 37.06        | 156.0158  | 3816.6653 | 9566.8886  | 3585.2065 | 0       | 2.981616667 | 40.49845    | 1.143225    |
| 30           | 39.71        | 151.98    | 4348.91   | 10639.87   | 4690.56   | 0.00    | 2.86        | 38.30       | 1.08        |
| 32           | 42.35        | 141.6697  | 4708.2602 | 10505.9377 | 4508.1092 | 0       | 3.1888      | 40.48745    | 0           |
| 34           | 45           | 154.4144  | 4393.6221 | 9574.9951  | 4606.746  | 0       | 3.2291      | 45.19645    | 1.0623      |
| 36           | 47.65        | 139.3115  | 4375.9246 | 9951.1893  | 4286.5207 | 0       | 3.1509      | 40.7653     | 0           |
| 38           | 50.29        | 151.739   | 3910.7609 | 9128.4608  | 3876.3428 | 0       | 3.04655     | 39.9029     | 0           |
| 40           | 52.94        | 148.0978  | 4220.5937 | 9898.4719  | 4188.7764 | 0       | 2.6535      | 34.0888     | 0           |
| 42           | 55.59        | 165.2947  | 4235.3782 | 9989.5979  | 4056.3738 | 0       | 3.1699      | 42.83235    | 0.87895     |
| 44           | 58.24        | 329.9332  | 1056.7096 | 2448.8508  | 1088.4953 | 0       | 3.11655     | 43.09155    | 1.1585      |
| 46           | 60.88        | 162.2024  | 4587.4324 | 10477.3483 | 4343.341  | 0       | 3.2206      | 44.04355    | 0.9092      |
| 48           | 63.53        | 189.809   | 4635.1505 | 10834.2101 | 4763.9469 | 0       | 3.2032      | 43.3516     | 0.99125     |
| 50           | 66.18        | 153.5966  | 4786.4785 | 11260.082  | 4842.6791 | 0       | 3.10075     | 43.9528     | 0.978       |
| 52           | 68.82        | 130.4877  | 4980.3638 | 11602.2167 | 4934.6486 | 0       | 2.636733333 | 37.33285    | 0.8283      |
| 54           | 71.47        | 73.902    | 2402.7456 | 5557.5091  | 2404.5891 | 0       | 3.24575     | 43.9295     | 0.9223      |
| 56           | 74.12        | 1082.8239 | 6178.9168 | 5724.1821  | 2885.927  | 0       | 3.15845     | 43.2526     | 0.9101      |
| 58           | 76.76        | 517.212   | 4895.5013 | 5630.1148  | 2741.5526 | 0       | 3.2216      | 46.52125    | 0.79175     |
| 60           | 79.41        | 409.3477  | 5249.4606 | 5277.2332  | 2486.7762 | 0       | 3.2616      | 46.03605    | 0.9666      |
| 62           | 82.06        | 265.9076  | 4482.5072 | 5450.5803  | 2368.2776 | 0       | 2.6513      | 39.2856     | 0.828225    |
| 64           | 84.71        | 110.116   | 6604.304  | 6871.752   | 3039.407  | 0       | 3.20765     | 40.00335    | 1.4805      |
| 66           | 87.35        | 102.592   | 6011.708  | 5085.296   | 2851.574  | 0       | 3.2713      | 39.0061     | 1.44695     |
| 67           | 88.68        | 71.923    | 5580.229  | 6107.745   | 2593.93   | 0       | 3.18755     | 37.2862     | 2.4135      |
| 68           | 90           |           |           |            |           |         |             |             |             |
| 100          | 100          | 45.814    | 53215.984 | 53420.516  | 24825.679 | 0       | 3.07285     | 37.77735    | 1.26945     |
| 103          | 103          | 32.171    | 20844.163 | 21294.178  | 10981.182 | 0       | 3.0997      | 37.17505    | 1.64045     |
| 107          | 107          | 281.484   | 5282.605  | 4705.72    | 2827.281  | 0       | 3.3801      | 38.87203333 | 1.434775    |
| 111          | 111          | 112.441   | 24934.416 | 24934.968  | 11619.185 | 0       | 2.69555     | 32.6847     | 1.3078      |
| 115          | 115          | 240.506   | 20521.022 | 22336.114  | 9961.298  | 0       | 3.06295     | 36.42445    | 1.95225     |
| 119          | 119          | 0         | 14697.369 | 15569.855  | 6062.52   | 0       | 3.2061      | 35.9895     | 1.72565     |
| 123          | 123          | 51.453    | 9314.769  | 10019.542  | 4718.55   | 0       | 2.6093      | 36.715      | 1.237375    |
| 127          | 127          | 79.966    | 10634.255 | 11671.188  | 5494.908  | 0       | 2.23605     | 34.11865    | 1.3632      |
| 131          | 131          | 64.281    | 9407.696  | 8835.367   | 4581.303  | 0       | 1.6914      | 20.9163     | 0.7786      |
| 135          | 135          | 72.172    | 10478.842 | 10644.038  | 4808.023  | 0       | 2.4382      | 30.4138     | 0.8642      |
| 139          | 139          | 636.761   | 4993.991  | 4116.864   | 2162.565  | 0       | 2.79815     | 37.1863     | 1.02815     |
| 143          | 143          | 0         | 8477.561  | 8622.855   | 3765.875  | 0       | 2.51065     | 35.15065    | 0.9284      |
| 147          | 147          | 1518.059  | 11020.284 | 9698.804   | 5076.911  | 0       | 3.4647      | 38.70855    | 0.98485     |
| 151          | 151          | 0         | 5537.88   | 6787.247   | 3146.361  | 106.804 | 2.76075     | 40.6015     | 1.2834      |
| 154          | 154          | 2710.279  | 0         | 0          | 0         | 977.032 | 2.844475    | 37.0703     | 0.836125    |

| Sample depth | Actual depth | Ti       | Pb 206   | Pb 207   | Pb 208   | Bi      | N(%)     | C(%)        | S(%)     |
|--------------|--------------|----------|----------|----------|----------|---------|----------|-------------|----------|
| 155          | 155          | 1603.424 | 1002.201 | 90.892   | 395.409  | 726.873 |          |             |          |
| 159          | 159          | 1542.727 | 9209.586 | 8704.814 | 4716.781 | 822.836 | 2.5499   | 28.76065    | 1.2377   |
| 163          | 163          | 1336.926 | 0        | 0        | 0        | 571.438 | 3.24595  | 38.4885     | 1.292025 |
| 167          | 167          | 278.926  | 4803.328 | 4132.022 | 2236.524 | 219.043 | 3.54604  | 39.77458    | 1.33346  |
| 171          | 171          | 298.159  | 3395.363 | 1539.656 | 1461.925 | 197.751 | 3.110275 | 37.35375    | 1.3085   |
| 175          | 175          | 205.803  | 4277.154 | 4193.044 | 2040.406 | 109.87  | 1.91755  | 19.3407     | 0.55435  |
| 179          | 179          | 182.957  | 4497.803 | 4352.655 | 2382.903 | 129.994 | 3.7218   | 39.56955    | 1.363    |
| 183          | 183          | 802.383  | 0        | 0        | 63.889   | 44.649  | 3.0486   | 35.4387     | 1.552425 |
| 187          | 187          | 1168.723 | 6617.218 | 5920.081 | 3376.651 | 77.849  | 3.68     | 37.105      | 1.235    |
| 195          | 195          | 494.081  | 1016.658 | 811.383  | 526.68   | 26.813  | 2.562    | 33.9272     | 1.2694   |
| 199          | 199          | 763.231  | 0        | 0        | 0        | 33.467  | 3.64745  | 34.13       | 1.29145  |
| 203          | 203          | 885.031  | 0        | 0        | 0        | 133.31  | 3.53     | 36.93       | 1.35     |
| 207          | 207          | 88.296   | 0        | 0        | 0        | 0       | 3.1309   | 34.4249     | 1.3445   |
| 211          | 211          | 244.169  | 0        | 0        | 0        | 33.458  | 3.1671   | 40.72235    | 1.1568   |
| 215          | 215          | 122.526  | 0        | 0        | 0        | 2.239   | 3.36435  | 40.9198     | 1.3464   |
| 219          | 219          | 0        | 0        | 0        | 0        | 7.442   | 3.01     | 32.82       | 1.495    |
| 223          | 223          | 0        | 0        | 0        | 0        | 0       | 2.744525 | 33.24706667 | 1.58715  |
| 227          | 227          | 171.818  | 0        | 0        | 0        | 0       | 2.175    | 25.545      | 3.075    |
| 231          | 231          | 80.829   | 0        | 0        | 0        | 0       | 2.445    | 29.44       | 1.61     |
| 235          | 235          | 44.162   | 0        | 0        | 0        | 0       | 1.38     | 17.59       | 1.205    |
| 239          | 239          | 12.238   | 0        | 0        | 0        | 8.965   | 1.39535  | 15.5755     | 0.727    |
| 243          | 243          | 0        | 0        | 0        | 0        | 0       | 0        | 18.5987     | 0.81395  |
| 247          | 247          | 0        | 0        | 0        | 0        | 4.48    | 1.6453   | 25.0876     | 1.1222   |
| 251          | 251          | 0        | 0        | 0        | 0        | 11.202  | 2.20555  | 14.24355    | 0.6479   |
| 255          | 255          | 0        | 0        | 0        | 0        | 66.235  | 1.3585   | 14.80875    | 0.83295  |
| 259          | 259          | 0        | 0        | 0        | 0        | 0       | 1.3679   | 15.89025    | 1.03335  |
| 263          | 263          | 225.502  | 0        | 0        | 0        | 0       | 1.46325  | 15.89025    | 1.03335  |
| 267.5        | 267.5        | 0        | 0        | 0        | 0        | 38.065  | 0.8901   | 9.6045      | 0.4821   |
| 271          | 271          | 0        | 0        | 0        | 0        | 0       | 0.9625   | 12.16705    | 1.291    |
| 275.5        | 275.5        | 0        | 0        | 0        | 0        | 0       | 1.13305  | 13.77085    | 0.9424   |
| 279          | 279          | 0        | 0        | 0        | 0        | 0       | 1.6908   | 22.4363     | 1.31215  |
| 283          | 283          | 0        | 0        | 0        | 0        | 0       | 1.68215  | 21.24495    | 2.1034   |
| 287          | 287          | 0        | 0        | 0        | 0        | 0       | 1.82865  | 21.09195    | 1.91575  |
| 289          | 289          | 0        | 0        | 0        | 0        | 0       | 0.64125  | 17.0535     | 1.73855  |
|              |              |          |          |          |          |         | 0.53405  | 6.00425     | 0.3873   |

| MAIVK   | RUN 1    |         |         | RUN 2    |         |         | RUN 3    |         |         | Average  |           |          |
|---------|----------|---------|---------|----------|---------|---------|----------|---------|---------|----------|-----------|----------|
|         | Nitrogen | Carbon  | Sulphur | Nitrogen | Carbon  | Sulphur | Nitrogen | Carbon  | Sulphur | Nitrogen | Carbon    | Sulphur  |
| 0-1     | 2.6715   | 38.3343 | 0.6935  |          |         |         |          |         |         | 2.65075  | 38.09985  | 0.71885  |
|         | 2.63     | 37.8654 | 0.7442  |          |         |         |          |         |         |          |           |          |
| 2-3i    | 3.0827   | 39.3411 |         | 3.14     | 44.14   | 0       | 2.8684   | 38.4216 | 0.9162  | 3.03     | 38.79     | 0.91     |
|         | 3.06     | 39.39   |         | 3.13     | 41.24   | 0.84    | 2.92     | 38.02   | 0.91    |          |           |          |
| 4-5i    | 3.14     | 44.13   | 0.9268  |          |         |         |          |         |         | 3.14     | 44.41     | 0.91105  |
|         | 3.13     | 44.68   | 0.8953  |          |         |         |          |         |         |          |           |          |
| 6 7ii   | 3.1777   | 41.1869 |         | 3.24     | 42.57   | 0       |          |         |         | 3.18     | 41.92     | 0        |
|         | 3.17     | 41.20   |         | 3.16     | 42.71   | 1.00    |          |         |         |          |           |          |
| 8-9i    | 3.2463   | 42.2222 |         | 3.02     | 36.16   |         | 3.083    | 39.6762 | 1.0573  | 3.12     | 40.986625 | 1.0316   |
|         | 3.2894   | 42.7746 |         | 3.10     | 37.44   | 0.8014  | 3.0045   | 39.2735 | 1.0059  |          |           |          |
| 10-11i  | 3.1537   | 40.9214 |         | 3.19     | 38.05   |         |          |         |         | 3.19     | 39.61     | 0        |
|         | 3.1308   | 40.7776 |         | 3.27     | 38.70   |         |          |         |         |          |           |          |
| 12-13i  | 3.0195   | 41.8707 | 1.1105  | 2.92     | 38.63   | 1.2796  | 2.7425   | 38.1617 | 1.0695  | 2.93     | 38.26     | 1.16     |
|         | 3.1273   | 43.0725 | 1.1611  | 2.75     | 38.74   | 1.2299  | 3.0106   | 37.5098 | 1.1344  |          |           |          |
| 14-15   | 3.1296   | 39.8813 |         | 3.03     | 36.39   |         | 2.9971   | 37.7844 | 1.1443  | 3.05     | 38.68     | 1.15     |
|         | 3.0886   | 39.4007 |         | 3.05     | 35.56   |         | 3.0077   | 37.6341 | 1.1527  |          |           |          |
| 16-17   | 3.2068   | 44.0397 | 1.1252  |          |         |         |          |         |         | 3.17075  | 43.77175  | 1.12775  |
|         | 3.1347   | 43.5038 | 1.1303  |          |         |         |          |         |         |          |           |          |
| 18-19ii | 3.1489   | 40.8985 |         |          |         |         |          |         |         | 3.16885  | 41.20165  |          |
|         | 3.1888   | 41.5048 |         |          |         |         |          |         |         |          |           |          |
| 20-21i  | 3.1209   | 44.635  | 1.2393  |          |         |         |          |         |         | 3.1233   | 44.5742   | 1.20695  |
|         | 3.1257   | 44.5134 | 1.1746  |          |         |         |          |         |         |          |           |          |
| 22-23ii | 3.0099   | 38.0817 |         |          |         |         |          |         |         | 3.00715  | 38.03995  |          |
|         | 3.0044   | 37.9982 |         |          |         |         |          |         |         |          |           |          |
| 24-25i  | 3.2074   | 44.0849 | 1.0658  |          |         |         |          |         |         | 3.2205   | 44.10795  | 1.02915  |
|         | 3.2336   | 44.131  | 0.9925  |          |         |         |          |         |         |          |           |          |
| 26-27i  | 3.1771   | 43.9341 | 1.1789  |          |         |         |          |         |         | 3.1611   | 43.61025  | 1.23435  |
|         | 3.1451   | 43.2864 | 1.2898  |          |         |         |          |         |         |          |           |          |
| 28-29i  | 3.1262   | 41.5876 |         | 2.75     | 40.7798 | 1.3302  | 2.8914   | 40.9855 | 0.9364  | 2.98     | 40.49845  | 1.143225 |
|         | 3.0495   | 40.282  |         | 3.0632   | 39.5667 | 1.2068  | 3.0092   | 39.9465 | 1.0995  |          |           |          |
| 30-31ii | 3.0729   | 43.1548 | 1.0103  | 2.6058   | 38.4332 | 1.0258  |          |         |         | 2.85895  | 38.3049   | 1.081425 |
|         | 3.0166   | 42.1316 | 1.1365  | 2.7405   | 38.1766 | 1.1531  |          |         |         |          |           |          |
| 32-33i  | 3.1483   | 40.0146 |         |          |         |         |          |         |         | 3.1888   | 40.48745  |          |
|         | 3.2293   | 40.9603 |         |          |         |         |          |         |         |          |           |          |
| 34-35ii | 3.2314   | 44.7247 | 1.0207  |          |         |         |          |         |         | 3.2291   | 45.19645  | 1.0623   |
|         | 3.2268   | 45.6682 | 1.1039  |          |         |         |          |         |         |          |           |          |
| 36-37i  | 3.1509   | 40.5492 |         |          |         |         |          |         |         | 3.1509   | 40.7653   |          |
|         | 3.1509   | 40.9814 |         |          |         |         |          |         |         |          |           |          |
| 38-39ii | 3.0396   | 39.8451 |         |          |         |         |          |         |         | 3.04655  | 39.9029   |          |
|         | 3.0535   | 39.9607 |         |          |         |         |          |         |         |          |           |          |
| 40-41ii | 2.6376   | 33.8501 |         |          |         |         |          |         |         | 2.6535   | 34.0888   |          |
|         | 2.6694   | 34.3275 |         |          |         |         |          |         |         |          |           |          |
| 42-43ii | 3.1859   | 42.6644 | 0.9024  |          |         |         |          |         |         | 3.1699   | 42.83235  | 0.87895  |
|         | 3.1539   | 43.0003 | 0.8555  |          |         |         |          |         |         |          |           |          |
| 44-45ii | 3.1212   | 43.2675 | 1.1749  |          |         |         |          |         |         | 3.11655  | 43.09155  | 1.1585   |
|         | 3.1119   | 42.9156 | 1.1421  |          |         |         |          |         |         |          |           |          |
| 46-47ii | 3.2294   | 44.4446 | 0.9366  |          |         |         |          |         |         | 3.2206   | 44.04355  | 0.9092   |
|         | 3.2118   | 43.6425 | 0.8818  |          |         |         |          |         |         |          |           |          |
| 48-49ii | 3.2125   | 43.2304 | 0.9582  |          |         |         |          |         |         | 3.2032   | 43.3516   | 0.99125  |
|         | 3.1939   | 43.4728 | 1.0243  |          |         |         |          |         |         |          |           |          |
| 50-51   | 3.1058   | 43.8372 | 0.9337  |          |         |         |          |         |         | 3.10075  | 43.9528   | 0.978    |
|         | 3.0957   | 44.0684 | 1.0223  |          |         |         |          |         |         |          |           |          |
| 52-53ii | 2.7744   | 41.6116 | 0.75    | 2.52     | 37.2601 | 0.9643  | 2.5976   | 36.2003 | 0.7347  | 2.64     | 37.33285  | 0.83     |
|         | 2.7674   | 40.3605 | 0.8647  | 2.4798   | 37.4056 | 0.9114  | 2.6796   | 35.7397 | 0.7447  |          |           |          |
| 54-55   | 3.2511   | 43.6067 | 0.9304  |          |         |         |          |         |         | 3.24575  | 43.9295   | 0.9223   |
|         | 3.2404   | 44.2523 | 0.9142  |          |         |         |          |         |         |          |           |          |
| 56-57i  | 3.1815   | 43.7787 | 0.8769  |          |         |         |          |         |         | 3.15845  | 43.2526   | 0.9101   |
|         | 3.1354   | 42.7265 | 0.9433  |          |         |         |          |         |         |          |           |          |
| 58 59   | 3.2182   | 46.7848 | 0.8027  |          |         |         |          |         |         | 3.2216   | 46.52125  | 0.79175  |
|         | 3.225    | 46.2577 | 0.7808  |          |         |         |          |         |         |          |           |          |
| 60 61   | 3.2835   | 46.1074 | 0.9703  |          |         |         |          |         |         | 3.2616   | 46.03605  | 0.9666   |
|         | 3.2397   | 45.9647 | 0.9629  |          |         |         |          |         |         |          |           |          |
| 62 63   | 2.7382   | 44.5247 | 0.8483  | 3.29     | 40.3551 | 1.4658  | 2.5906   | 38.6528 | 0.877   | 2.65     | 39.2856   | 0.828225 |
|         | 2.6806   | 43.3459 | 0.766   | 3.1233   | 39.6516 | 1.4952  | 2.5958   | 38.4829 | 0.8216  |          |           |          |
| 64-65i  | 3.292    | 40.3551 | 1.4658  |          |         |         |          |         |         | 3.20765  | 40.00335  | 1.4805   |
|         | 3.1233   | 39.6516 | 1.4952  |          |         |         |          |         |         |          |           |          |
| 66-67   | 3.314    | 38.95   | 1.4579  |          |         |         |          |         |         | 3.2713   | 39.0061   | 1.44695  |
|         | 3.2286   | 39.0622 | 1.436   |          |         |         |          |         |         |          |           |          |
| 67-68   | 3.2542   | 37.0716 | 3.3153  |          |         |         |          |         |         | 3.18755  | 37.2862   | 2.4135   |

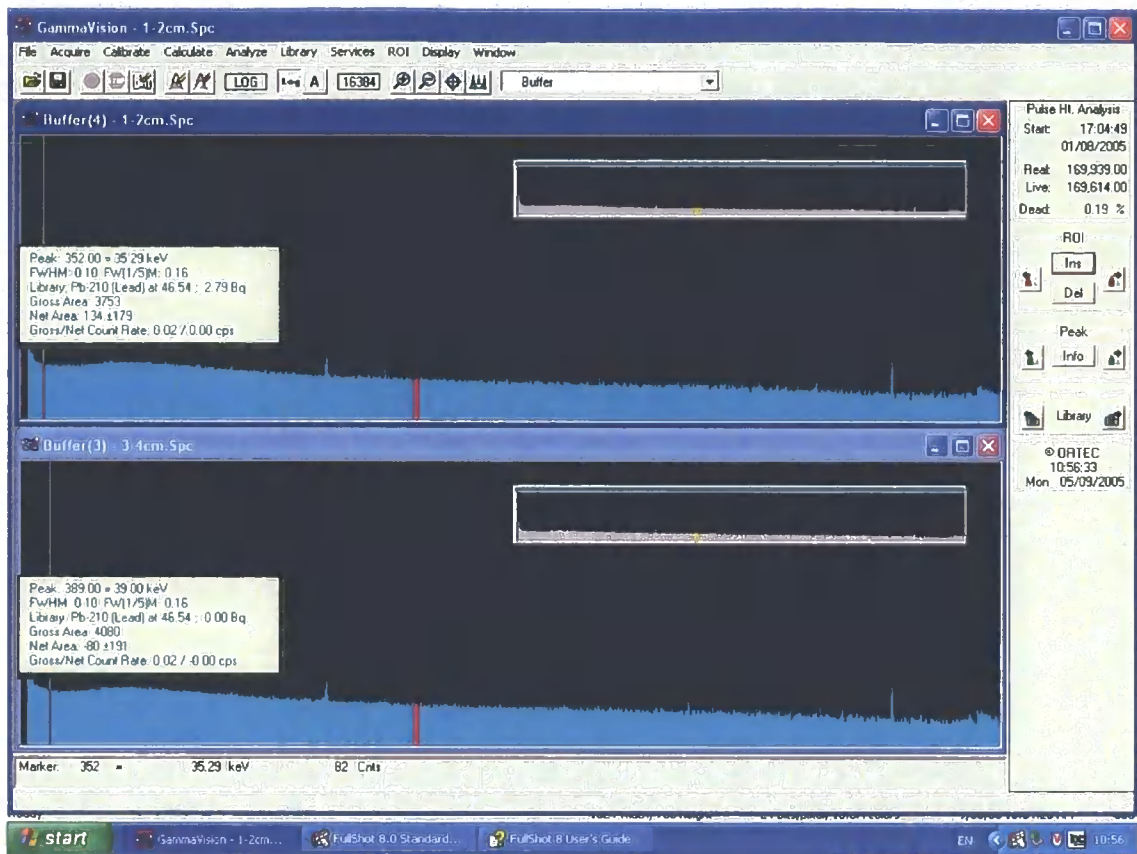
| MAIVK    | RUN 1    |         |         | RUN 2    |         |         | RUN 3    |         |         | Average  |             |          |
|----------|----------|---------|---------|----------|---------|---------|----------|---------|---------|----------|-------------|----------|
|          | Nitrogen | Carbon  | Sulphur | Nitrogen | Carbon  | Sulphur | Nitrogen | Carbon  | Sulphur | Nitrogen | Carbon      | Sulphur  |
|          | 3.1209   | 37.5008 | 1.5117  |          |         |         |          |         |         |          |             |          |
| HUM3     |          |         |         |          |         |         |          |         |         |          |             |          |
| 0-1      | 3.0848   | 37.7234 | 1.3102  |          |         |         |          |         |         | 3.07285  | 37.77735    | 1.26945  |
|          | 3.0609   | 37.8313 | 1.2287  |          |         |         |          |         |         |          |             |          |
| 3 4      | 3.0862   | 37.3964 | 1.6621  |          |         |         |          |         |         | 3.0997   | 37.17505    | 1.64045  |
|          | 3.1132   | 36.9537 | 1.6188  |          |         |         |          |         |         |          |             |          |
| 7 8      | 3.1056   | 38.7687 | 1.5613  | 3.2155   | 39.0413 | 1.2284  |          |         |         | 3.3801   | 38.87203333 | 1.434775 |
|          | 3.7167   | 44.1991 | 1.7562  | 3.4826   | 38.8061 | 1.1932  |          |         |         |          |             |          |
| 11 12    | 2.6079   | 32.6762 | 1.3182  |          |         |         |          |         |         | 2.69555  | 32.6847     | 1.3078   |
|          | 2.7832   | 32.6932 | 1.2974  |          |         |         |          |         |         |          |             |          |
| 15 16    | 3.0176   | 36.4453 | 1.9011  |          |         |         |          |         |         | 3.06295  | 36.42445    | 1.95225  |
|          | 3.1083   | 36.4036 | 2.0034  |          |         |         |          |         |         |          |             |          |
| 19 20    | 3.1458   | 36.0681 | 1.6979  |          |         |         |          |         |         | 3.2061   | 35.9895     | 1.72565  |
|          | 3.2664   | 35.9109 | 1.7534  |          |         |         |          |         |         |          |             |          |
| 23 24    | 2.4504   | 35.1877 | 1.4574  | 2.6388   | 36.8312 | 0.9577  |          |         |         | 2.6093   | 36.715      | 1.237375 |
|          | 2.7388   | 36.6179 | 1.5124  | 2.6092   | 36.6959 | 1.022   |          |         |         |          |             |          |
| 27 28    | 2.2219   | 34.5551 | 1.552   |          |         |         |          |         |         | 2.23605  | 34.11865    | 1.3632   |
|          | 2.2502   | 33.6822 | 1.1744  |          |         |         |          |         |         |          |             |          |
| 31 32i   | 1.70     | 20.86   | 0.79    |          |         |         |          |         |         | 1.6914   | 20.9163     | 0.7786   |
|          | 1.68     | 20.98   | 0.77    |          |         |         |          |         |         |          |             |          |
| 35 36    | 2.43     | 30.69   | 0.83    |          |         |         |          |         |         | 2.4382   | 30.4138     | 0.8642   |
|          | 2.44     | 30.14   | 0.90    |          |         |         |          |         |         |          |             |          |
| 39 40i   | 2.81     | 37.08   | 1.02    |          |         |         |          |         |         | 2.79815  | 37.1863     | 1.02815  |
|          | 2.79     | 37.29   | 1.04    |          |         |         |          |         |         |          |             |          |
| 43 44    | 2.56     | 35.21   | 0.94    |          |         |         |          |         |         | 2.51065  | 35.15065    | 0.9284   |
|          | 2.47     | 35.09   | 0.92    |          |         |         |          |         |         |          |             |          |
| 47 48i   | 3.48     | 38.60   | 0.98    |          |         |         |          |         |         | 3.4647   | 38.70855    | 0.98495  |
|          | 3.45     | 38.81   | 0.99    |          |         |         |          |         |         |          |             |          |
| 51 52    | 2.95     | 41.16   |         | 2.69     | 40.5346 | 1.2545  |          |         |         | 2.76     | 40.60       | 1.28     |
|          | 2.78     | 38.22   |         | 2.6253   | 40.6684 | 1.3123  |          |         |         |          |             |          |
| 54 55i   | 3.61     | 45.77   | 1.56    | 2.9705   | 37.2564 | 0.7843  | 2.64     | 36.8904 | 0.7613  | 2.844475 | 37.0703     | 0.836125 |
|          | 3.12     | 35.64   | 1.59    | 2.9032   | 37.448  | 0.9718  | 2.8642   | 36.6864 | 0.8271  |          |             |          |
| 59 60    | 2.52     | 28.94   | 1.2443  |          |         |         |          |         |         | 2.55     | 28.76065    | 1.2377   |
|          | 2.58     | 28.58   | 1.2311  |          |         |         |          |         |         |          |             |          |
| 63 64i   | 3.5247   | 39.3722 | 1.2967  | 2.941    | 38.9147 | 1.2999  |          |         |         | 3.24595  | 38.4885     | 1.292025 |
|          | 3.3943   | 37.526  | 1.2365  | 3.1238   | 38.1411 | 1.335   |          |         |         |          |             |          |
| 67 68    | 3.7173   | 40.1915 | 1.4148  | 2.54     | 34.0437 | 1.0828  | 3.3745   | 40.034  | 1.1267  | 3.54604  | 39.77458    | 1.33346  |
|          | 3.698    | 39.3829 |         | 3.3735   | 39.636  | 1.6896  | 3.5669   | 39.6285 | 1.3534  |          |             |          |
| 71 72i   | 3.2324   | 36.0684 |         | 3.0692   | 37.3165 | 1.2803  |          |         |         | 3.110275 | 37.35375    | 1.3085   |
|          | 3.0863   | 34.2877 |         | 3.0532   | 37.391  | 1.3367  |          |         |         |          |             |          |
| 75 76    | 1.9222   | 19.4386 | 0.5623  |          |         |         |          |         |         | 1.91755  | 19.3407     | 0.55435  |
|          | 1.9129   | 19.2428 | 0.5464  |          |         |         |          |         |         |          |             |          |
| 79 80i   | 3.7202   | 36.63   |         | 3.5587   | 39.6132 | 1.3317  |          |         |         | 3.7218   | 39.56955    | 1.363    |
|          | 3.9383   | 38.1716 |         | 3.67     | 39.5259 | 1.3943  |          |         |         |          |             |          |
| 83 84    | 3.24     | 35.22   | 1.58    | 2.9163   | 35.7635 | 1.6073  |          |         |         | 3.0486   | 35.4387     | 1.552425 |
|          | 3.12     | 33.71   | 1.53    | 2.9181   | 35.3326 | 1.4924  |          |         |         |          |             |          |
| 87 88i   | 3.63     | 36.93   | 1.24    |          |         |         |          |         |         | 3.68     | 37.105      | 1.235    |
|          | 3.73     | 37.28   | 1.23    |          |         |         |          |         |         |          |             |          |
| 95 96i   | 3.0377   | 34.1517 | 1.2775  |          |         |         |          |         |         | 2.562    | 33.9272     | 1.2694   |
|          | 2.0863   | 33.7027 | 1.2613  |          |         |         |          |         |         |          |             |          |
| 99 100   | 3.6886   | 34.0282 | 1.3394  |          |         |         |          |         |         | 3.64745  | 34.13       | 1.29145  |
|          | 3.6063   | 34.2318 | 1.2435  |          |         |         |          |         |         |          |             |          |
| 103 104i | 3.53     | 36.66   | 1.33    |          |         |         |          |         |         | 3.53     | 36.93       | 1.35     |
|          | 3.53     | 37.2    | 1.37    |          |         |         |          |         |         |          |             |          |
| 107 108  | 3.172    | 34.4975 | 1.3317  |          |         |         |          |         |         | 3.1309   | 34.4249     | 1.3445   |
|          | 3.0898   | 34.3523 | 1.3573  |          |         |         |          |         |         |          |             |          |
| 111 112i | 2.9669   | 41.1335 | 1.1796  |          |         |         |          |         |         | 3.1671   | 40.72235    | 1.1568   |
|          | 3.3673   | 40.3112 | 1.134   |          |         |         |          |         |         |          |             |          |
| 115 116  | 3.365    | 41.1998 | 1.4339  |          |         |         |          |         |         | 3.36435  | 40.9198     | 1.3464   |
|          | 3.3637   | 40.6398 | 1.2589  |          |         |         |          |         |         |          |             |          |
| 119 120i | 2.98     | 32.09   | 1.45    |          |         |         |          |         |         | 3.01     | 32.82       | 1.495    |
|          | 3.04     | 33.55   | 1.54    |          |         |         |          |         |         |          |             |          |
| 123 124  | 2.89     | 33.17   | 1.75    | 2.5887   | 33.2644 | 1.534   |          |         |         | 2.744525 | 33.24706667 | 1.58715  |
|          | 2.84     | 31.28   | 1.58    | 2.6594   | 33.3068 | 1.4846  |          |         |         |          |             |          |
| 127 128i | 2.19     | 25.53   | 2.96    |          |         |         |          |         |         | 2.175    | 25.545      | 3.075    |
|          | 2.16     | 25.56   | 3.19    |          |         |         |          |         |         |          |             |          |
| 131 132  | 2.4      | 29.5    | 1.7     |          |         |         |          |         |         | 2.445    | 29.44       | 1.61     |
|          | 2.49     | 29.38   | 1.52    |          |         |         |          |         |         |          |             |          |
| 135 136i | 1.39     | 17.69   | 1.23    |          |         |         |          |         |         | 1.38     | 17.59       | 1.205    |



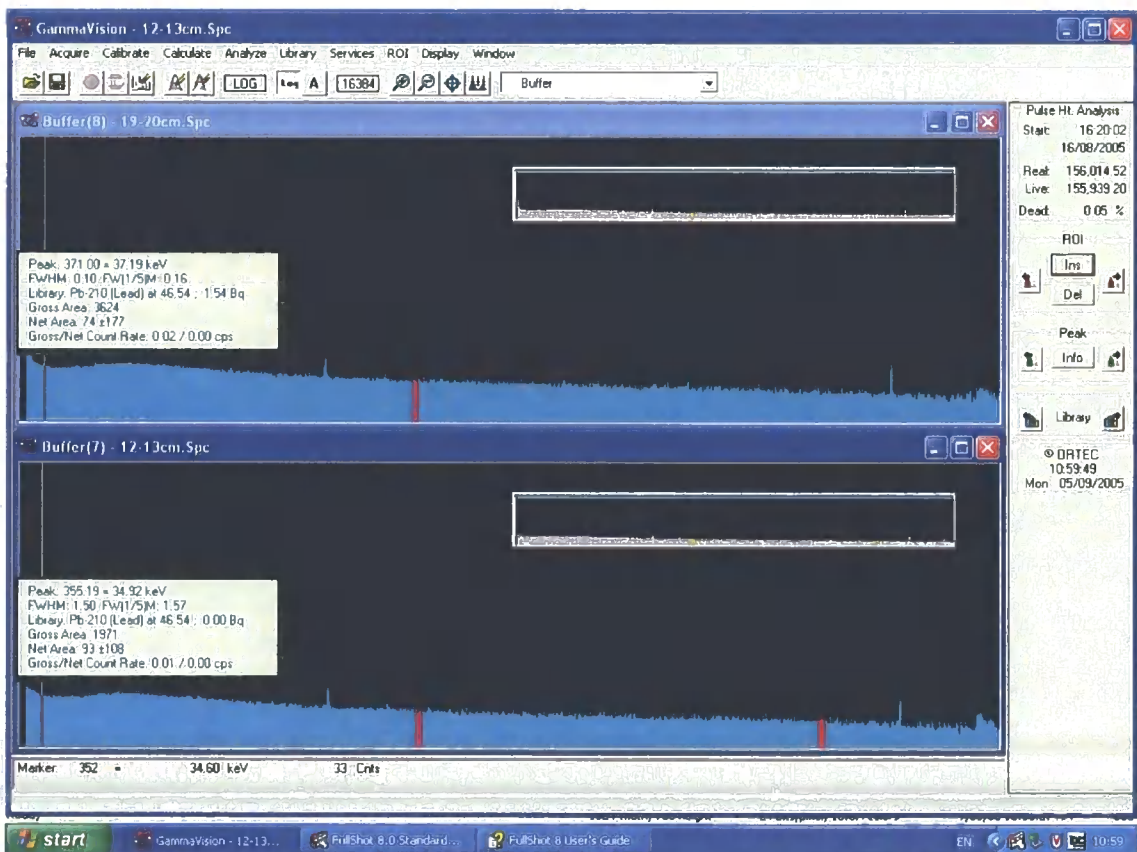
## Appendix 3

### $^{210}\text{Pb}$ and $^{137}\text{Cs}$ results

As the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  analysis was unsuccessful, a full set of results is not possible. This appendix shows the actual counts of a number of different samples through the core. If  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  had been present within these samples, peaks would have been observed. Although small peaks are observed in some of the samples, these peaks are consistent in every sample and are part of the background level. The line and the label indicate the position where the peak in the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  concentration would be. All sample numbers are depths in the MAIV/K core before taking into account shrinkage of the core.



Samples 1-2cm and 3-4cm.



Samples 19-20cm and 12-13cm.



Sample 14-15cm and 10-11cm. This indicates the count at peaks, however these peaks do not occur at the correct position for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  and are fluctuations in the background level.

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