

Project: AFI 4/02

**BEHAVIOUR OF TRACE ELEMENT AND ISOTOPE RATIOS OF SEA-ICE BRINE AND
MICROALGAE**

Principal Investigator: Prof. Harry Elderfield (University of Cambridge)

Co-Investigators: Dr Rosalind Rickaby (University of Oxford)

Dr Raja Ganeshram (University of Edinburgh)

Location: Rothera research station and Ryder Bay

Field Personnel: Damien Carson¹ (PhD student)
Katharine hendry² (PhD student)

¹School of Geosciences, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JW

²Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR

Introduction:

Biological productivity and subsequent carbon dioxide drawdown in the Southern Ocean are important for global climate. Productivity in the coastal regions off the West Antarctic Peninsula (WAP) is dominated by highly seasonal phytoplankton blooms, mostly comprising diatoms. The WAP has experienced the most rapid warming in recent decades.

The Southern Ocean features prominently in many hypotheses developed to explain past drops in atmospheric carbon dioxide during Quaternary glaciations. Critical to testing these hypotheses is our ability to reconstruct past conditions of Southern Ocean primary productivity, nutrient availability and utilisation based on isotopic and trace element proxies. One aspect of these proxy records not fully investigated is the extent to which they are influenced by materials formed within sea ice, an environment vastly different from that of the open water column. Most proxies are calibrated for open ocean settings, so materials produced within sea ice could potentially confound proxy-based reconstructions of water column conditions. Detailed studies on sea ice material are lacking for most isotopic and trace element proxies used in the Southern Ocean.

It is vital to understand both modern systems and the impact of past climate change on such biological productivity in order to assess future scenarios. The 2005-2006 field season was highly successful and will form a key part of both theses for Oxford and Edinburgh students.

Project objectives:

The aims of the project at Oxford University are as follows: 1) seasonal variation of trace metal uptake (zinc, cadmium, aluminium) into diatom frustules and the impact on uptake of sea-ice and phytoplankton blooms within Ryder Bay 2) past changes in Marguerite Bay by using trace metal content of fossil diatoms as proxies for sea-ice and nutrient regimes.

The aims of the project at Edinburgh are to investigate how biogeochemical cycling in the near-shore sea ice environment influences high latitude geochemical proxies and

how export production relationships differ in the sea ice environment. This will be observed by assessing biogeochemical proxy signals ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, Ba, U, Ag) of nutrients and organic matter in sea ice compared to the open water column and following flux of this material in time series sediment traps located to two depths below the sampling site. Past changes in these proxy signals in Ryder Bay will also be investigated from box core material taken from the study site.

Rothera and Ryder Bay Sampling 2005-2006:

Sea-ice blocks, brine and underlying water samples were successfully collected by Paul Mann throughout the austral winter 2005. The sea-ice blocks collected and stored at -80°C were thawed during the summer and filtered and will be analysed along with the brine samples in the UK from June 2006.

The 2005/2006 field season ran from November 2005 to March 2006. The first few days at Rothera were occupied by field training comprising a refresher course on BAS modules 1-3 (field training) and module 6 (sea-ice training). After training was complete, sampling commenced. Laboratory procedures were similar to last season, with the addition of a Class 100 clean bench for trace metal work.

Hangar Cove was used as the early season sea-ice sampling site for safety reasons. Brine samples were collected by sack-hole drilling. Seawater samples were collected from under the sea-ice with the help of the dive team. Surface water samples were also collected in March and filtered in a similar manner for a comparison. Surface sediment samples were collected from Hangar Cove by Matt Brown, Daniel Smale and Paul Mann.

Boat training and water sampling from RaTS CTD site 1 and 2 commenced in late December when the sea-ice finally cleared from Ryder Bay on boxing day 2005. Water sampling was carried out using a plastic pump and cleaned silicone tubing. The time series was highly successful, with excellent coverage and temporal resolution throughout the summer.

For a map of sampling sites, refer to Figure 1.



Figure 1: Map of Ryder Bay. Stars show major sampling sites.

Additional samples were taken from Honeybucket, just offshore from Rothera Point, for diatom cleaning experiments in Oxford.

Cruise JR136/137 on the RRS *James Clark Ross*:

Cruise JR136/137 was delayed until mid-February due to extensive sea ice cover in Ryder Bay. Box coring was postponed and the cruise subsequently focused on water sampling and CTD casts. Sediment trap moorings deployed in January 2005 were successfully recovered and redeployed.

A CTD transect was conducted across the mouth of Marguerite Bay (it was the intention to cover the entire mouth, but sea ice prevented this from happening), and through the trough leading towards the mooring sites, see Figure 2. These casts were used to sample nutrients (NO_3^- , NO_2^- , Si(OH)_4), nutrient isotopes ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}$), bulk organic POC/PON and bulk organic $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PON}}$.

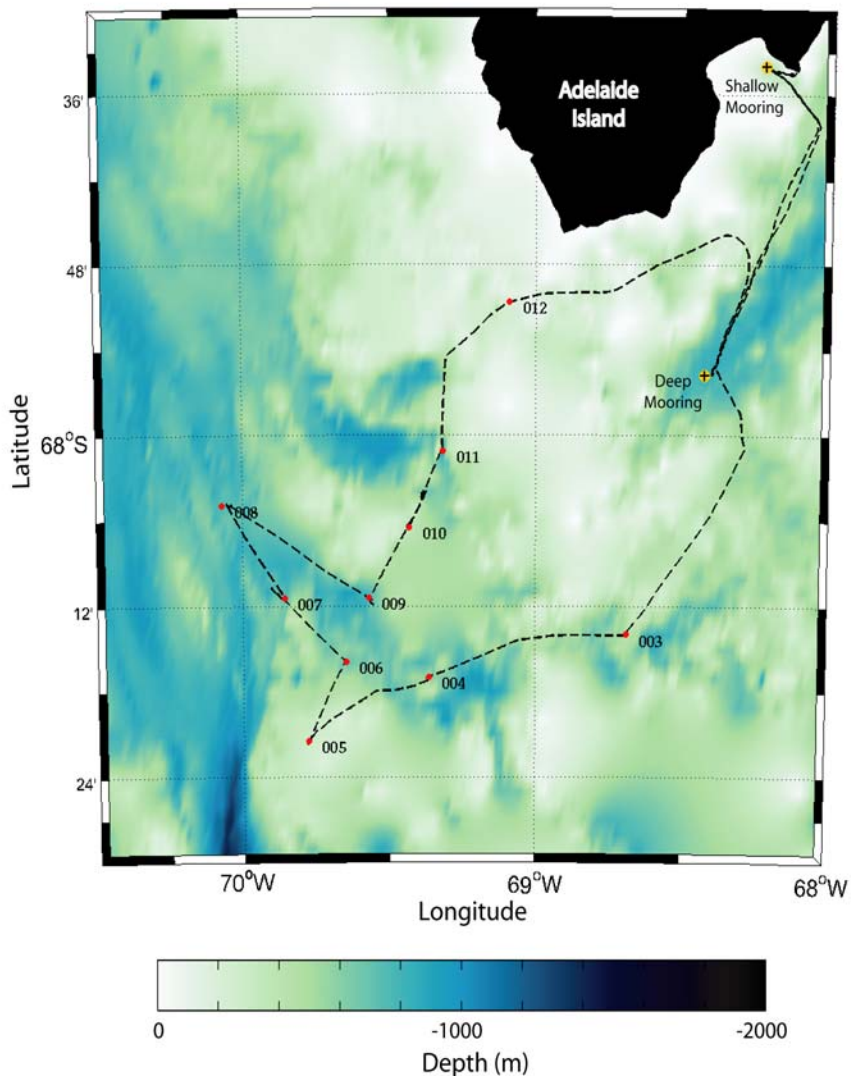


Figure 2. Cruise track of JCR cruise 136/137

Some Preliminary Data from field season 2004-2005:

RaTS Results

Nitrate (NO_3^-) and nitrite (NO_2^-) concentrations from sea ice and RaTS water samples were analysed at The University of Edinburgh, using standard autoanalyser techniques. Ammonium concentrations were determined at Rothera using the phenol method employed by the RaTS programme. For nutrient profiles, see Figure 3. Silicic acid analyses were conducted at Oxford (Figure 4).

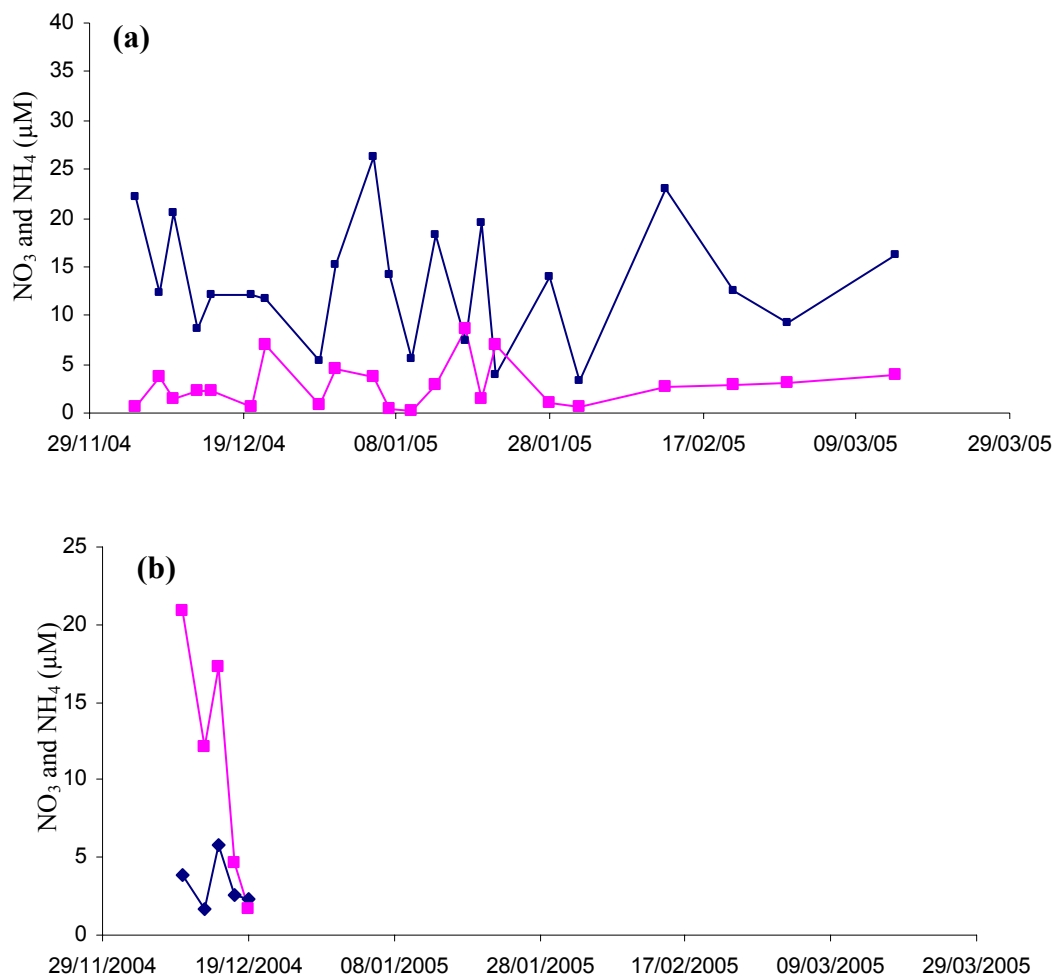


Figure 3. (a) Nutrient profiles from RaTS site and (b) sea ice during the 2004/2005 field season. Blue profiles are nitrate and purple profiles are ammonium (D. Carson, Edinburgh).

The RaTS site shows typical seasonal variability in nutrients, whereas the sea ice has atypical nutrient conditions where ammonium was the dominant nutrient. This could be due to remineralisation of PON and the affinity of sea ice diatoms for ammonium as a nutrient source. Isotopes of DIC, NO_3^- and NH_4^+ should highlight why we see this atypical nutrient inventory in sea ice.

Seasonal variations in silicic acid in Ryder Bay, 2004-2005

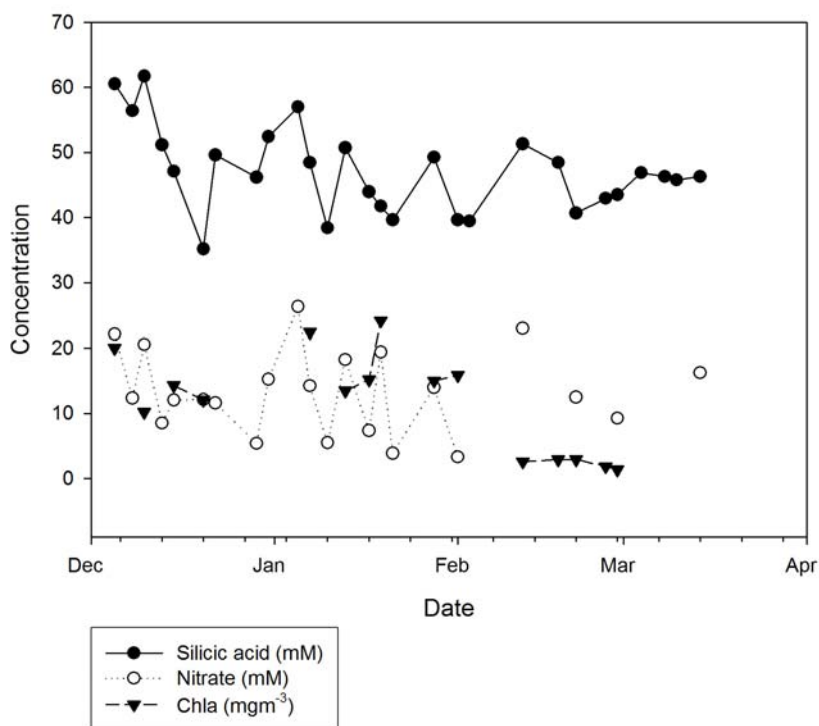


Figure 4: Variations in silicic acid in Ryder Bay, summer 2004-2005 (K. Hendry, Oxford).

The elemental (POC/PON) and stable isotopic ($\delta^{13}\text{C}_{\text{org}}/\delta^{15}\text{N}$) composition of organic matter from sea ice and surface waters are presented in Figure 5. In Figure 5 (a) and (b), the time series shows higher POC concentrations in sea ice compared to the surface waters, whereas PON is similar in sea ice compared to surface waters. Figure 5 (c) depicts flux weighted averages of the C/N data and shows very clearly the differences in organic matter content and stable isotopic composition between the two environments.

It appears that the PON in sea ice is likely subject to higher rates of remineralisation than the POC, suggested by the high C/N ratio of bulk organic matter. PON is known to be more labile and easily remineralised compared to POC as about 80% of PON from planktonic organic matter is in the form of amino acids, which are the most labile fraction of sedimentary organic material. This interpretation is also backed by the dominance of NH_4^+ in sea ice brine (see Figure 3.), remineralised PON is transformed to NH_4^+ and can be preferentially used as a nitrogen source by plankton in the Southern Ocean.

Analysis and interpretation of the stable isotopic composition of DIC, NO_3^- and NH_4^+ should explain why we see the aforementioned conditions in sea ice and highlight which nutrients are preferentially used.

Analysis of diatom bound $\delta^{15}\text{N}$ (method under development) should also highlight whether the heavier isotopic signal in sea ice is produced during plankton formation or subsequent diagenesis. This question is yet to be addressed in the literature.

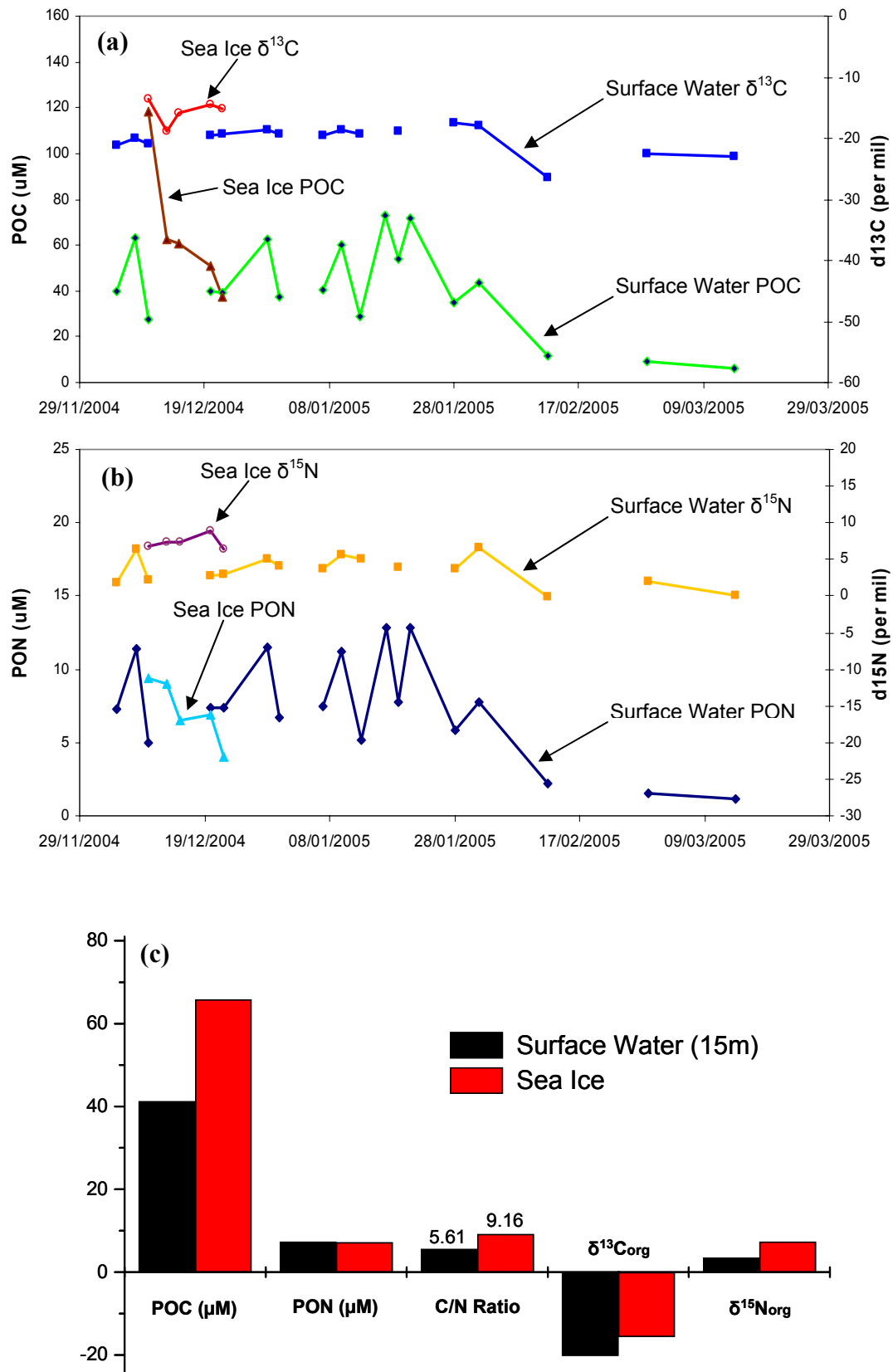


Figure 5. 2004/2005 field season (a) Bulk POC and $\delta^{13}\text{C}$ from sea ice and surface water at the RaTS site and (b) Bulk PON and $\delta^{15}\text{N}$ from sea ice and surface water at the RaTS site and (c) Flux weighted averages of elements and isotopes from sea ice and surface waters (D. Carson, Edinburgh).

In addition, Kate Hendry established her methodology for trace metal analyses. Initial results indicate no significant trace metal laboratory contamination.

Marguerite Bay Results:

Analysis on a box core taken from Marguerite Bay in January 2005 was conducted in Oxford by 1) adapting a method for extracting fossil diatoms from sediments (MORLEY et al., 2004); 2) carrying out a diatom population analysis on core BC 390 (Figure 4).

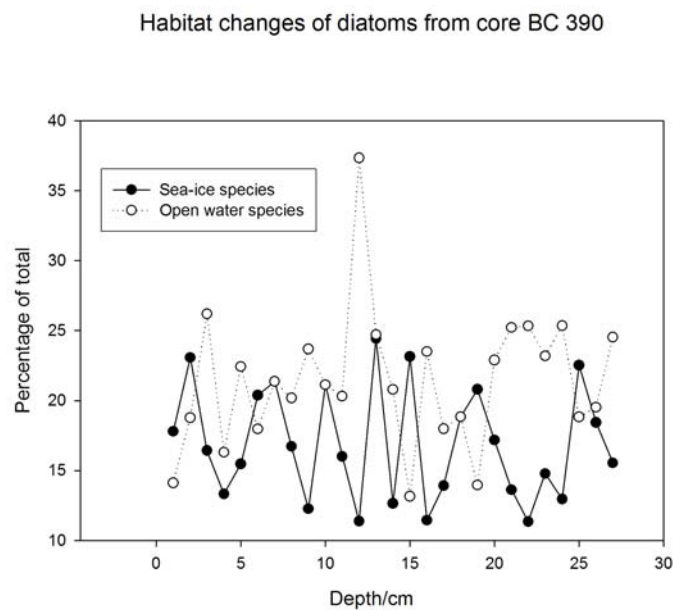
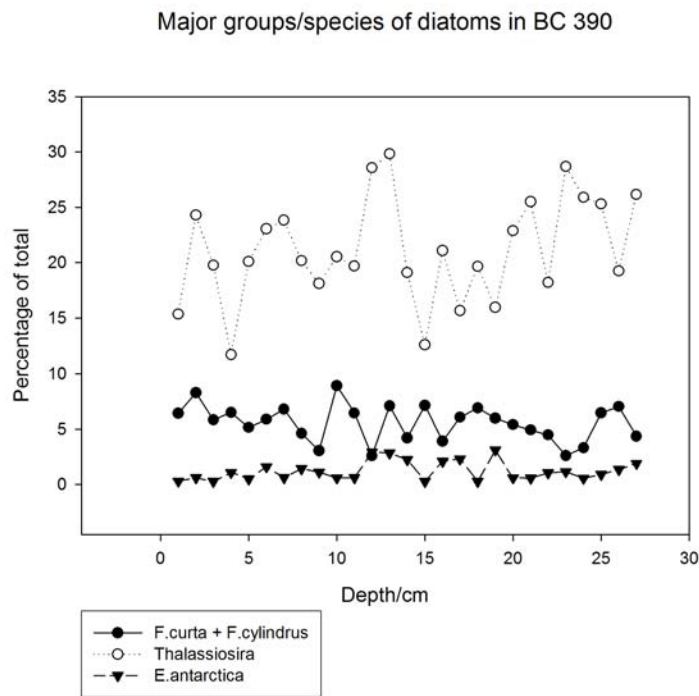


Figure 4. (a) Population variations of important diatom groups for box core BC 390 (b) Habitat changes of diatoms from core BC390 (K. Hendry, Oxford).

At least 300 diatoms were counted per slide, including *Chaetoceros* resting spores. *Fragilariopsis curta* and *cylindrus* are sea-ice species; *Thalassiosira* species are generally open water; *Eucampia antarctica* is frequently used as a stratigraphic marker. The low levels of *E.antarctica* suggest that the core does not extend as far back as the Last Glacial Maximum

Future work:

There will be one month spent at Rothera Research Station from November 2006 until December 2006. This will be spent sampling more sea ice for work at Edinburgh and Oxford. Two cruises on the RRS James Clark Ross and RRS Ernest Shackleton will follow in December and March for the purpose of box coring and turning over the sediment trap moorings.

In the UK, lab work will involve working through and analysing all samples collected from field seasons, including sea ice, surface water, sediment trap and box core samples.

The final aim will be to achieve publication of final results, often in partnership with BAS and other AFI projects.

Acknowledgments:

Many thanks to Paul Mann, Helen Rossetti, Keith Weston, Matt Brown, Dan Smale, Samia Mantoura and everyone at Rothera Research Station. Thanks also to the Masters and Crew of the RRS *James Clark Ross*.