The Changing Arctic Ocean Seafloor (ChAOS)
- The organic geochemistry contribution

Dr Geoff Abbott and Mark Stevenson

- **Quantify** organic matter *quantity*, *source* and *reactivity* from **contrasting regions** of ice cover to assess its impact on carbon and nutrient *recycling* and *burial*.
- **Quantify** *marine* versus *terrestrial* OM sources using:
  - C/N ratios
  - Lignin phenols (^{13}C labelled TMAH)
  - *n*-alkanes, *n*-alkanols, *n*-alkanoic acids

The Changing Arctic Ocean Seafloor (ChAOS)

Module 1

What is the total *amount* and macronutrient stoichiometry of OM *delivered* to the seafloor?

Down-core and sea ice gradient - TOC, TIC, TN

What is the dominant *source* of OM *delivered* to the seafloor?

C/N, lignin phenols, *n*-alkanes, *n*-alkanols, *n*-alkanoic acids

ToF-SIMS & GC-MS

What is the *reactivity/bioavailability* of OM *delivered* to the seafloor?

XPS – bonding of C & N, sterols: stanols, lignin reactivity

The Changing Arctic Ocean Seafloor (ChAOS)

Module 1

What is the *fate* of OM below the *sediment-water interface*?

Comparisons between organic markers down-core (up to ~40 cm depth)

Comparisons of organic markers with inorganic proxies, microbial ecology & pore water chemistry

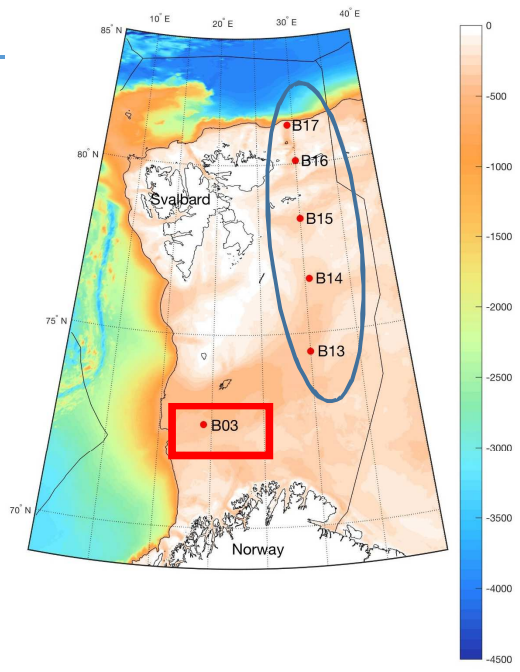
Sampling sites

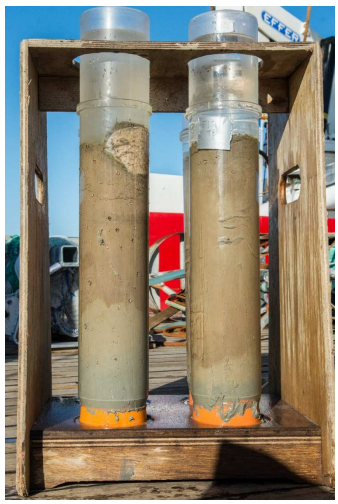
ChAOS Stations B17 – B14

priority

30° E north – south transect

B03 – potential future extension





Each ChAOS station with 3 replicates, sampled 21 – 36 cm depth

Organic geochemistry analyses

Module 1

Q1 – TOC, TIC, TN

Q2 – C/N

Lignin/*Sphagnum* phenols, *n*-alkanes, *n*-alkanols, *n*-alkanoic acids

Q3 – XPS to quantify bulk sediments and assess bonding of C and N
Degraded/undegraded lignin phenols with ^{13}C TMAH
Stenols to stanols ratio
Decarboxylation of long chain *n*-alkanoic acids to form long-chain *n*-alkanes

Sample preparation

Collection

Freeze drying

Sediment homogenization

Foil lined cap

To reduce plasticiser contamination:
Freeze dry in solvent cleaned glass vials, with foil coated tops

ChAOS Sample Inventory

~150 samples stored at -80 °C

~300 samples stored at -20 °C

Bulk carbon & nitrogen

1. Analysis of bulk C, TOC, TIC & TN

LECO TOC analyser

- Acidification with HCL

↓

Removal of carbonates

TC−TOC = TIC

Elementar vario MAX CNS

C, N & S

First samples = 1.5 to 2% C, N = ~0.1%, S = ~0.1%

Analysis approach – B13 to B17 one replicate ~150 samples → Extend to the replicates ~450 samples

Lipid extraction comparison

2. Comparison of Soxhlet, Soxtec, ACE and ultrasonication

Soxhlet method

Soxtec

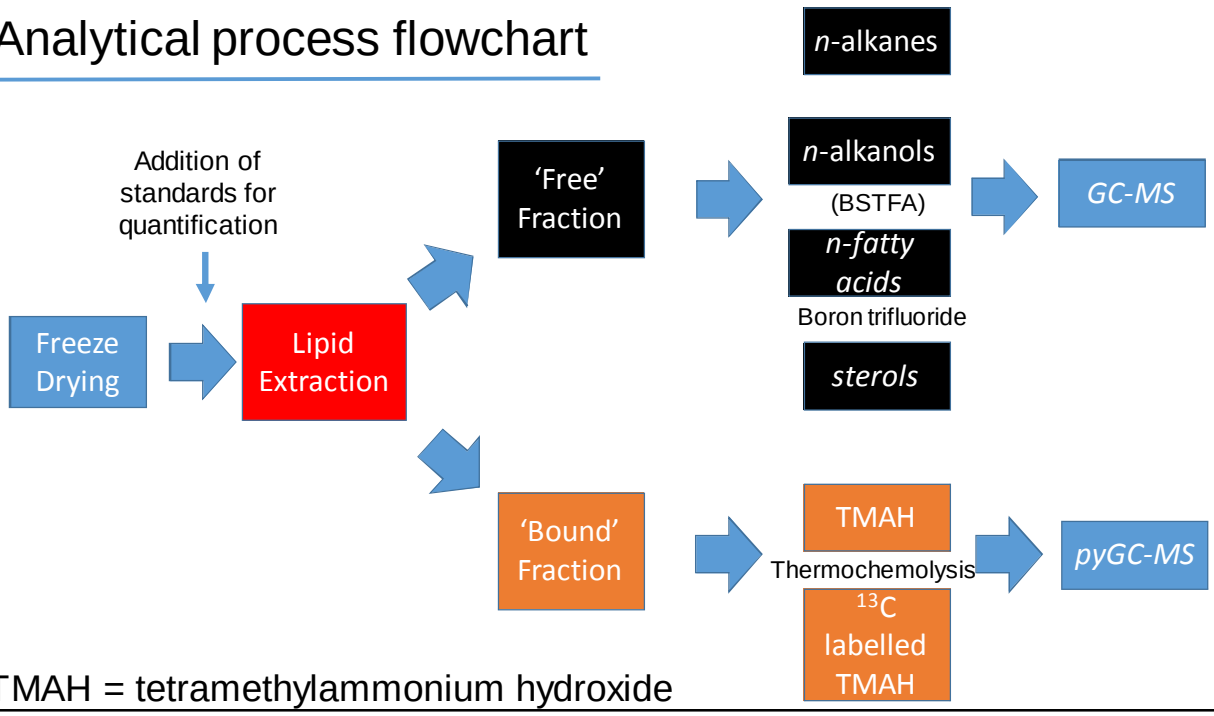
Ultrasonic bath

Accelerated Solvent Extraction (ASE)

Trial multiple methods on one core to identify most efficient extraction method for Barents Sea sediments → Select 1 method of extraction to enable comparison between sites

Based on TOC, TC profiles select ~10 samples per core

Analytical process flowchart



TMAH = tetramethylammonium hydroxide

Lipid extraction – 'bound' fraction

3. Analysis of lignin phenols using pyrolysis GC-MS

Priority – first use py/GC-MS on 'bound' fraction as requires minimal further preparation

Trial both unlabelled and ^{13}C-labelled tetramethylammonium hydroxide (TMAH) (e.g. Abbott et al., 2013)

Aim: - Help quantify the terrestrial contribution at each location & how this might differ along the sea-ice gradient

Pyrolysis pyroprobe and GC-MS

Lipid extraction – 'free' fraction

4. Analysis of *n*-alkanes, *n*-alkanols and *n*-alkanoic acids

Either entire neutral extract & acid extract
(if all compounds amenable together on GC-MS)

or

Separate into sub-fractions using silica columns

Neutral fraction:
Aliphatic hydrocarbons
Aromatic hydrocarbons
Ketones and aldehydes
n-Alkanols plus sterols (BTSFA)

Acid fraction:
n-Alkanoic acid methyl esters

GC-MS

Potential extensions – Compound specific $\delta^{13}C$

- Lipid extracts (*n*-alkanes, *n*-fatty acids) can be run on the GC-IRMS for $\delta^{13}C$, to enable tracking of carbon source into sediments

Understand carbon flows as sediment matures + How carbon flow pathways differ between stations

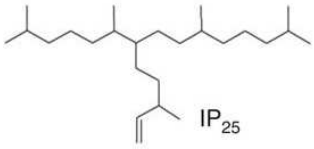
Are terrestrial inputs processed on the seafloor?

GC-C-IRMS

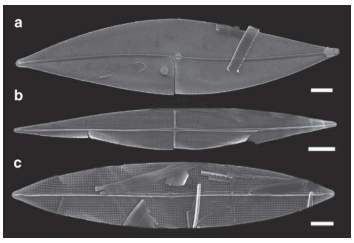
Highly branched isoprenoids – IP_{25}

- Branched isoprenoids could be good sea ice indicators:

IP_{25} – Arctic sea ice proxy
(e.g. Belt et al., 2014)



When did sea ice decline at the station?



Pleurosigma stuxbergii var. rhomboides
Haslea crucigeroides
Haslea kjellmanii

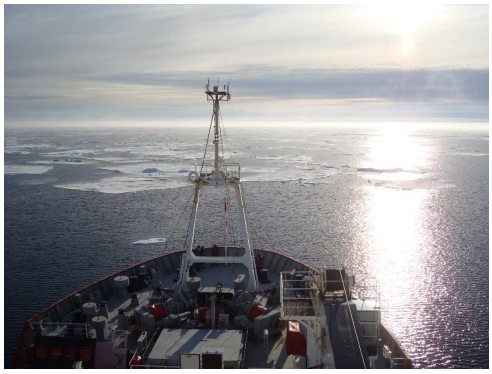
IP_{25}-producing diatom species (Brown et al., 2014)

Potential extensions – Alkenones

- Alkenones are likely to be present and could be a good proxy of temperature:

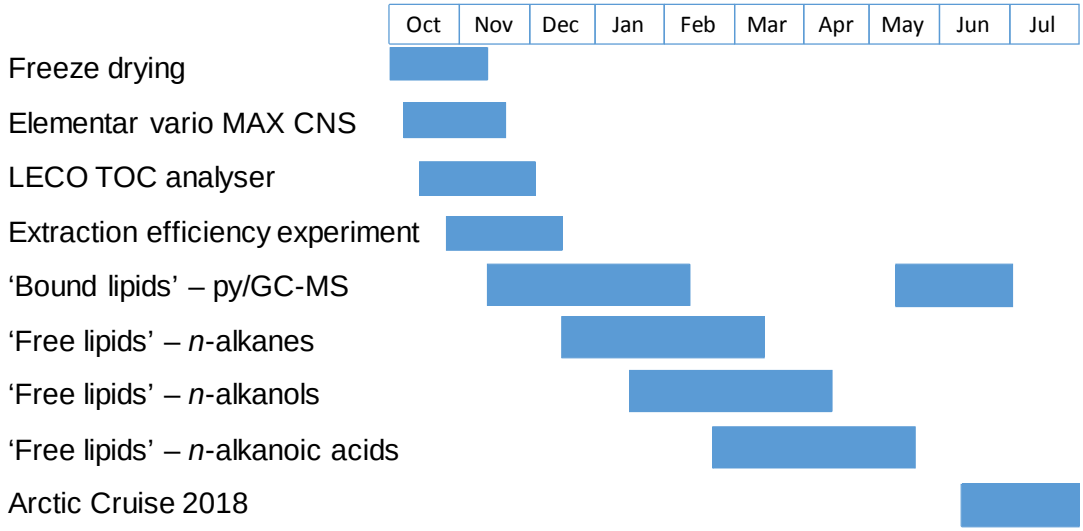
$U^{K'}_{37} = C_{37:2}/(C_{37:2} + C_{37:3})$ alkenone index
(e.g. Eglinton et al., 1992)

- Sourced from phytoplankton class – *Prymnesiophyceae*
Long-chain unsaturated methyl and ethyl *n-ketones*



37:3 alkenone - $C_{37}H_{68}O$

Timeline



There will be some cross over of analyses – as appropriate depending on kit availability