

Australian participation in KEOPS:

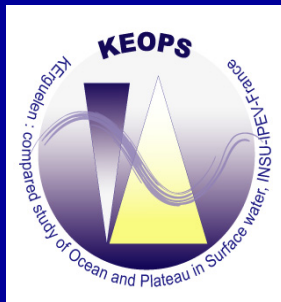
1. Science

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Overview

- Slide 3. List of participants and their research areas
- Slide 4. List of major equipment
- Slides 5-17. Brief descriptions of research projects
- Slides 18-19. References cited – available as .pdfs

Australian participation

- Tom Trull (ACE CRC)
 - $\delta^{13}\text{C}$ -DIC, $\delta^{13}\text{C}$ -POC, $\delta^{15}\text{N}$ -NO₃, $\delta^{15}\text{N}$ -PON
 - size-fractionated suspended particles, sinking particles
 - contribution to new/recycled/exported production estimates
- Andrew Bowie (ACE CRC)
 - size-fractionated dissolved and particulate iron, contribution to iron budgets, tracers for aerosol iron inputs
- Brian Griffiths (CSIRO)
 - ¹⁴C primary production, bio-optics, CDOM samples
- Leanne Armand (CSIRO)
 - diatom taxonomy, fluorescent tracers of species-specific silicification
- Lisette Robertson (ACE CRC)
 - trace-metal clean “fish”, pump, and trap deployments; sample processing

Australian major equipment

- National Facility Trace Metal Clean Laboratory Container
- ACE/AAD/CMR Radioisotope Laboratory Container
- Trace-metal clean towed “fish” underway sampler
- Trace-metal polycarbonate hydrocast samplers (10x6L)
- Submersible pump for large volume particle sampling in top 120m - returns 50 L/min to deck via hose, distributed to 5x142mm filter rigs for size fractions (200, 55, 20, 5, 1 microns) - water available to others - Ba, REE, DMSP, POC/²³⁴Th, etc.
- Free-drifting surface tethered, Argo-GPS, McLane 13-cup sediment trap for sinking particles (trace-metal clean). Particles available to others - Ba, REE, DMSP, POC/²³⁴Th (*This replaces the earlier proposed moored sediment trap*).

Trull science synopsis 1

- Identification of phytoplankton responsible for export
- Contribution to KEOPS Objective 2.2 “Export”
- Method:
 - Comparison of ^{13}C -POC compositions of different size fractions (200, 55, 20, 5, 1 μm) with ^{13}C -DIC enrichments in surface waters produced by seasonal DIC depletion
- Reference:
 - Trull, T.W., and L. Armand, Deep-Sea Research II, 48 (11/12), 2655-2680, 2001
- Samples:
 - ^{13}C -DIC profiles from CTD Niskins, 6 sites, 12 depths, 250mls
 - ^{13}C -DIC surface samples from CTD Niskins, ~30 sites, 250mls
 - ^{13}C -POC samples on size-fractions from submersible pump, 6 sites, 5 depths
 - ^{13}C -POC samples from free-drifting conical-trap
- Cooperation:
 - Conical-trap and size-fractionated suspended particles available for Ba, POC/ ^{234}Th , etc., Comparison to DIC and POC measurements (OISO, F.Diaz)

Trull science synopsis 2

- Examination of new versus recycled production
- Contribution to KEOPS Objective 3. “Biogeochemical Processes”
- **Method:**
 - Comparison of ^{15}N - NO_3 and ^{15}N -PON compositions to distinguish new vs. recycled production, and possible response to Fe - new production is ^{15}N rich, and increases with Fe availability.
- **Reference:**
 - Karsh, K.L., T.W. Trull, M.J. Lourey, and D.M. Sigman, *Limnology and Oceanography*, 48, 1058-1068, 2003.
- **Samples:**
 - ^{15}N - NO_3 profiles from CTD Niskins, 6 sites, 12 depths, 250mls
 - ^{15}N - NO_3 surface samples from CTD Niskins, ~30 sites, 250mls
 - ^{15}N -PON samples on size-fractions from submersible pump, 6 sites, 5 depths
 - ^{15}N -PON samples from free-drifting conical-trap
- **Cooperation:**
 - Comparison to ^{15}N incubation-based estimates of new and recycled production
 - Benefits from ammonium determinations – if these are planned?

Trull science synopsis 3

- Calibration of ^{13}C and ^{15}N signatures of biological pump strength
- Contribution to KEOPS Objective 2.2 “Export”
- Contribution to KEOPS Objectives 3. “Biogeochemical Processes”
- **Method:**
 - Comparison of ^{15}N N-PON compositions with seasonal nitrate depletion
 - Comparison of ^{13}C -POC compositions with surface pCO_2 values
 - Comparison of Fe-rich KEOPS results with Fe-poor SAZ results
- **References:**
 - Lourey, M.J., T.W. Trull, and D.M. Sigman, *Global Biogeochemical Cycles*, 17 (3), 1081, doi:10.1029/2002GB001973, 2003
 - Lourey, M.J., T.W. Trull, and B. Tilbrook, *DSR I*, 51 (2), 281-305, 2004
- **Samples:**
 - Conical-Trap and size-fractionated suspended particles
- **Cooperation:**
 - Requires pCO_2 determinations from OISO team, and CTD nitrate analyses

Bowie science synopsis 1

- Size-fractionated filtration: soluble and colloidal iron distribution
- Extends preliminary iron distribution studies above the Kerguelen plateau
- Compare physical speciation: Kerguelen plateau & open Southern Ocean
- Lab-based aluminium measurements for use as tracer of aerosol iron
- Hypothesis:
 - #1: In productive waters above the Kerguelen plateau, colloidal iron dominates the dissolved pool
 - #2: During phytoplankton growth, the dominant form of dissolved iron shifts from soluble to colloidal species
- Contribution to KEOPS objectives:
 - 1: Which mechanisms are responsible for deep waters iron enrichment, and subsequent upward transfer to the surface layer?
 - 2: Aerosols as a source of iron to the ocean
 - 3: Remineralisation and iron speciation

Bowie science synopsis 2

- Soluble and colloidal iron distribution
- **Sampling**
 - Underway: near-surface water using polyurethane coated towed torpedo fish and trace metal clean pumping system
 - Water column: vertical profiling by hydrocast using trace metal clean Go-Flo bottles/polycarbonate samplers deployed off Kevlar hydroline
- **Processing and analysis**
 - Nitrogen gas over pressurisation, sequential filtration through 0.02 (Anotop), 0.2 and 0.4 micron filters
- **Analysis**
 - Shipboard flow injection with luminol chemiluminescence detection, (Bowie et al. 1998)
 - Aluminium by FIA-fluorescence

| <i>Defined Fe fraction</i> | <i>Size-fraction</i> |
|----------------------------|------------------------|
| Truly soluble | <0.02 μm |
| Colloidal | 0.02-0.4 μm |
| Dissolved | <0.4 μm |
| Total dissolvable | Unfiltered, TDFe |
| Labile particulate | Unfiltered - dissolved |

Bowie science synopsis 3

- Iron content & nutrient ratios (Fe:C) of suspended and sinking particles
 - Size-fractionated trace metal distribution in 4 fractions
- Removal of surface-bound iron from phytoplankton
 - Use of novel trace metal clean reagents (Tovar-Sanchez et al., 2003)
- Improvement of ecosystem structure within biogeochemical models
 - Mass balance of export enables us to close the iron budget
- Hypothesis:
 - #1: Iron is effectively removed from the dissolved (soluble) phase during bloom conditions and bound up in biogenic particles associated with large phytoplankton species
 - #2: Iron is retained in the mixed layer via efficient trophic cycling within the food-web, and Fe:C ratios increase due to alleviation of Fe limitation
 - #3: During bloom senescence, biogenic iron is exported to depth and predominantly associated with large sinking particles
- Contribution to KEOPS objectives:
 - #2.2: Quantification of carbon flux exported below the depth of the winter mixed layer.
 - #3: Remineralisation and iron speciation

Bowie science synopsis 4

- **Sampling: suspended particulate material**
 - Clean seawater supplied via towfish and/or polycarbonate hydrocast samplers
 - Sequential filtration through four 47 mm filters (210, 55, 20, 2 micron) held in a Teflon PFA stack (Savillex)
- **Sampling: sinking particulate material**
 - Free-floating time-series funnel-type sediment trap
 - 150-300 m (?) depth, sample collection every 3 days
 - Cups filled with a brine solution; organic poison used as a preservative
 - Material filtered through a sequence of size-fractionated filters housed in a polypropylene stack (see above)
- **Digestion and analysis**
 - Teflon PFA bombs (Savillex) using H_2O_2 (organics) and HNO_3/HF at 120°C for 4 h (marine particles)
 - High resolution ICP-MS of up to 10 elements

Griffiths science synopsis 1

- **P vs E Hypotheses:**
 - Primary production, photosynthetic parameters, and DOC production rates will be higher in areas naturally enriched with iron than non-enriched areas.
- **Methods: small-bottle, P vs E incubations**
(Griffiths et al, JGR 104(D17) 21649-21671,1999).
- **Sampling:**
 - Standard P vs E: 250ml from 6 depths in mixed layer, one depth below. Samples from CTD casts or trace-metal clean bottles.
 - DOC release rates: 500 ml from 2 depths in mixed layer, one below. Samples from CTD or trace-metal clean bottles.
 - One station per day
- **Cooperation or other data needed:**
 - Chlorophyll at each sampling depth; fluorometer profiles.
 - Production data available to other participants.
- **Contribution to KEOPS Objectives 2.2 and 3.1**

Griffiths science synopsis 2

- **Measurement:** Size-fractionated primary production by simulated in-situ deck incubations.
- **Hypothesis:**
 - Regions with naturally high iron will have higher gross and net primary production, and a higher portion of the primary production in the largest phytoplankton size classes.
- **Sampling:**
 - Incubations using water from six depths with about 2.5 litres per depth.
 - Gross (daytime) and 24 hour production to be measured.
 - Require water to be taken from CTD cast before dawn.
 - Need chlorophyll concentration for each depth (fluorometry?)
 - Provide deck incubator, but need 5-10 l minute⁻¹ seawater for cooling.
- **Method:** Standard JGOFS Protocol
- **Contribution to KEOPS Objectives 2.2 and 3.1**

Griffiths science synopsis 3

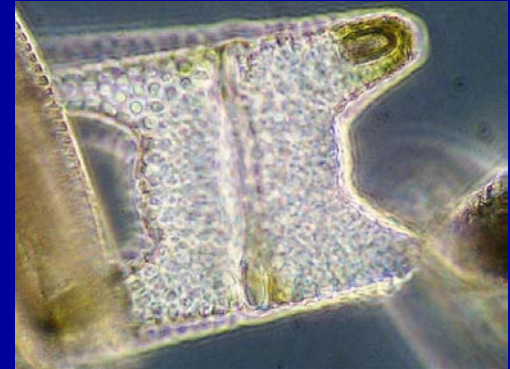
- **Nutrient limitation studies**
 - Contrast possible nutrient limitation, particularly silicate, in phytoplankton by measuring the fluorescence response to nutrient addition.
 - Determine if nutrient limitation is occurring in some of the OBEX incubation studies, or if nutrient limitation has relaxed following amendment treatments (possible collaboration area).
 - Experimental technique being developed.
 - Require 25 ml samples from CTD casts or incubation bottles.
- **Underway Measurements**
 - Distribution of CDOM in surface waters via fluorometry.
 - Determine contribution of CDOM to remotely sensed chlorophyll-a
 - Diel patterns in photosynthetic characteristics and fluorescence in surface waters in relation to PAR
 - More realistic representation of diel patterns in photosynthetic rate in models of primary production.
 - Sampling: need to be able to put two fluorometers and a Fast repetition-rate fluorometer in-line with thermosalinograph.
- **Contribution to KEOPS Objective 3.1**

Griffiths science synopsis 4

- Explore factors impacting on primary production models.
 - Diel patterns in photosynthetic parameters measured by P vs E and Fast repetition-rate fluorometer (FRRF) methods for $P^{b_{opt}}$ type primary production models.
 - Determine the contribution of coloured dissolved organic matter (CDOM) to remotely sensed chlorophyll-a.
 - Measure spectral absorbance of phytoplankton and FRRF methods for input into quantum yield type primary production models.
- **Sampling**
 - Photosynthetic parameters from ^{14}C small bottle incubations.
 - CDOM via continuous underway sampling or 100ml samples from CTD.
 - Spectral absorbance: 1-2 litres at 4 depths in the mixed layer (same depths as P vs E samples).
 - FRRF profiles on the CTD.
- **Cooperation**
 - Chlorophyll-a and pigments for the spectral absorbance samples.
 - Mounting FRRF and battery pack on the CTD rosette
 - The fraction of primary production in the largest phytoplankton size classes will be greatest in regions of highest iron concentration.
- **Contribution to KEOPS Objective 2.2**

Armand science synopsis 1

- Identification of Diatoms
- Contribution to KEOPS Objectives:
 - 3.1 Structure of Phytoplankton communities
 - 2.2 Export
- Method:
 - Qualitative assessment via semi or permanent smear slide analysis.
 - Quantitative assessment through lab-based silica selective treatments (based on Schrader and Gersonde, 1978) (restricted capacity, known volume sampling/splits required, pursued only in cooperation).
- Samples:
 - As provided by Australian and French team during various sampling protocols (eg. ~10-50ml per depth per CTD-max 3 depths, sediments 1cm³).
- Cooperation:



Please raise your anticipated needs for identification
or quantitative analysis now!

Armand science synopsis 2

- Silica Uptake Kinetic Experiments -
(under the Quéguiner program umbrella)
- Contribution to KEOPS Objectives:
 - 3.1 Structure of Phytoplankton communities
- Method and samples:
 - Under guidance of B. Quéguiner (LOB)
- Cooperation:
 - Dependent on EU funding.



References (available as .pdfs)

- Bowie A.R., Maldonado M.T., Frew R.D., Croot P.L., Achterberg E.P., Mantoura R.F.C., Worsfold P.J., Law C.S., Boyd P.W., 2001. The fate of added iron during a mesoscale fertilisation experiment in the Southern Ocean. *Deep-Sea Research II* 48, 2703-2743.
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- Trull, T.W., and L. Armand, Insights into Southern Ocean carbon export from the $d^{13}C$ of particles and dissolved inorganic carbon during the SOIREE iron fertilisation experiment, *Deep-Sea Research II*, 48 (11/12), 2655-2680, 2001.