

## 9. <sup>234</sup>Thorium and Stand Alone Pumps (SAPS)

### 9.1 <sup>234</sup>Th on D285

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Objective: To measure total (dissolved and particulate) thorium-234 as a proxy measurement of carbon export.

All major process stations were sampled: 15492 (M1), 15495 (M3), 15498 (M3), 15503 (M2), 15512 (M6), 15517 (M3), 15523 (M7), 15533 (M8E), 15539 (M8W), 15542 (M9). Also sampled the shake down station 15487 and station 15548.

Sample volume 10 litres.

Profiles from all major stations had 10 sampling depths with higher resolution in the top 200m and lower resolution down to ~500m.

When the thorium cast was considered to be significantly separated in time or space (or both) from the standard sCTD samples were also collected for POC/N and chlorophyll.

Salts also taken from Niskins allocated for thorium so that a value for uranium concentration can be derived.

A double precipitation was carried out on samples collected from station 15542 to estimate the extraction efficiency. This entails collecting the filtrate from the first precipitation and re-precipitating the filtrate to see if anymore <sup>234</sup>Th can be extracted.

Samples from station 15548 were all collected from 1000m to estimate the precision on the method.

Volume of seawater filtered: 1240 litres (1.24 metric tons)

#### Problems/Suggestions/Comments

When initially decanting concentrated ammonia in the fume hood it quickly became apparent that the filters in the fume hood were not suitable for ammonia. Stunk out the labs!! Risk assessment amended to dispense ammonia in a well ventilated space eg in the hanger. Solution: have filters that are capable of handling ammonia.

Originally we tried to collect the <sup>234</sup>Th samples from the main core sCTD at the shake down station (15492) but the water budget proved too tight, therefore it was decided to have a separate thorium cast. Only way to combine the thorium and sCTD casts would be to either have larger Niskins (if they do them) or sample fewer depths.

Having an extra cast for thorium allowed other parameters to gain opportunistic volumes of water, namely radium, which required high volumes of deep water. See radium cruise report for further details.

Claudia also took some samples from 20-40m. CO<sub>2</sub> samples taken at station 15495 and O<sub>2</sub> and CO<sub>2</sub> on station 15539.

Two <sup>234</sup>Th samples only totalled 5 litres in volume due to leaking Niskins.

Filtration procedure is very time consuming because only one sample can be filtered at a time, ~8h to filter 10 samples. The method could very easily be scaled up to process multiple samples at once.



Objective: to measure Carbon and Nitrogen export from  $^{234}\text{Th}$  and  $^{238}\text{U}$  disequilibria

Biological activity in surface waters drives the oceanic particle cycle, which in turn controls the scavenging of trace metals and sedimentation to the sea floor. Carbon fixation and carbon export is central to understanding oceanic productivity, and its long-term effect on atmospheric  $\text{CO}_2$  concentration. The particle-reactive radioisotope  $^{234}\text{Th}$  (half life 24.1 days) is often in disequilibrium with its parent nuclide  $^{238}\text{U}$  in surface ocean waters. This occurs because  $^{234}\text{Th}$  but not  $^{238}\text{U}$  partitions strongly onto particle surfaces and its removal on the sinking flux of material leads to radioactive disequilibrium. Consequently  $^{234}\text{Th}/^{238}\text{U}$  disequilibrium is potentially a powerful tool to study the downward flux of carbon in the ocean via sinking particles.

Knowledge of the integrated disequilibrium in the water column combined with a steady-state assumption and with the decay constant of  $^{234}\text{Th}$  yields an estimate for the flux of  $^{234}\text{Th}$  from the surface ocean caused by settling particles. To calculate the POC flux from the surface ocean, the ratio of POC to  $^{234}\text{Th}$  on sinking particles is multiplied by the estimated  $^{234}\text{Th}$  flux.

### Methods

Samples for thorium analysis were collected from the stainless steel CTD at various stations (see Table 1 for station positions). Ten litre water samples were collected from ten depths to 500m. The sampling distribution is concentrated in the surface 300m where a significant export of thorium on settling particles is expected to result in radioactive disequilibrium between thorium and uranium. The samples collected at 500m represent radioactive equilibrium between  $^{234}\text{Th}$  and  $^{238}\text{U}$ .

Total uranium is calculated from salinity and does not have to be measured independently.

Total  $^{234}\text{Th}$  is measured by adding potassium permanganate ( $\text{KMnO}_6$ ), manganese dichloride ( $\text{MnCl}_2$ ), and concentrated ammonia ( $\text{NH}_3$ ) to the 10 litre water sample. Dissolved and particulate  $^{234}\text{Th}$  is precipitated from the water as  $\text{MnO}_2$  precipitate within 8 hours. This precipitate is filtered onto 142mm  $0.8\mu\text{m}$  polycarbonate filters which are then folded in a reproducible way, wrapped in mylar foil and counted directly in a beta counter. Appropriate corrections are made for self-absorption of radiation due to the filter and for detector efficiencies  $<100\%$ , and corrections for  $^{234}\text{Th}$  decay and  $^{234}\text{Th}$  in growth from  $^{238}\text{U}$  decay since sampling.

The extraction efficiency of the precipitate as well as the precision and reproducibility of the method were tested at station 15632 where nine of the Niskin bottles allocated to thorium were fired at 1000m. Accuracy may be assessed by comparing the determined activity of total  $^{234}\text{Th}$  with the  $^{238}\text{U}$  activity at 1000m. Following the filtration of the precipitate, the filtered sea water is collected and the precipitation process is repeated to test whether all the thorium was removed from the sample by the first precipitate and hence determine the extraction efficiency of the precipitate.

At each of the thorium depths samples for particulate organic carbon (POC) and particulate organic nitrogen (PON) were filtered onto ashed GFF filters. Filters are stored frozen at -20°C for future analysis at the Southampton Oceanography Centre. These samples were collected in particular to determine how the ratio of total POC and PON to <sup>234</sup>Th changed through the water column.

The large particulate thorium fraction >50µm was sampled by deploying in-situ Stand Alone Pumps (SAP) at the bottom of the export layer. A 293mm 50µm nylon mesh was inserted into the filter holder of the SAP which was set to pump for 90 minutes. Once the SAP pumps are back on board the 60µm mesh is removed and rinsed with 1 litre of filtered thorium free sea water. The SAP sample is then split using a Fulsam sample splitter. 6/8<sup>ths</sup> of the sample is filtered onto 142mm 0.8µm polycarbonate filter for <sup>234</sup>Thorium. 1/16<sup>th</sup> of the sample is filtered onto a pre weighed GFF filter for POC and PON analysis. 1/16<sup>th</sup> is filtered onto a 20um polycarbonate filter for Biogenic Silica. 1/6<sup>th</sup> is stored in Lugols and Formalin for microscopy. 3x 5ml of 1/16<sup>th</sup> is filtered for Chlorophyll and the remainder of the 1/16<sup>th</sup> split is filtered for HPLC pigment analysis.

**Table 9.1 Thorium station positions on D286**

Station Number	Station Identifier	Date	Latitude	Longitude	SAPS Number	SAPS Depth
15554	M9	19/12/04	42° 59.80' S	47° 01.26 E	11	120m
15560	M10	20/12/04	44° 31.09' S	49° 59.51' E	12	110m
15574	M3	23/12/04	46° 04.84' S	51° 46.96' E	13	180m
15580	M5	27/12/04	45° 59.88' S	56° 09.10' E	15	125m
15590	M3	31/12/04	46° 03.74' S	51° 46.63' E	16	100m
15595	M6	03/01/05	48° 59.93' S	51° 32.27' E	17	120m
15603	M2	06/01/05	47° 47.57' S	52° 51.05' E	19	160m
15613	M3	09/01/05	46° 08.33' S	51° 51.25' E	20	80m
15620	M3	10/01/05	46° 01.56' S	51° 52.11' E	21	80m
15627	M3	12/01/05	46° 02.31' S	51° 57.44' E	23	80m
15632	M10	15/01/05	44° 30.09' S	49° 59.07' E	-	-

### 9.3 SAPS (Stand Alone Pump System)

Hélène Planquette, Paul Morris



Objective: to collect the particles that are sinking from the biologically productive mixed layer of the water column, in order to measure C and Fe export from the upper ocean.

The depth the SAPS were deployed at was determined on a case by case basis. Parameters we used to determine this depth were water temperature, fluorescence and transmission. We aimed to put the SAPS at a depth that would collect the sinking particles that were falling out of the biologically productive surface layers of the water column. So the SAPS were deployed below the thermal mixed layer, below the bulk of the chlorophyll and below where the transmission starts to increase, and gave ourselves about a 20m margin of error below these features.

Approximate depth of deployment ranged from 150-225m. (Tables 9.2 and 9.3)

SAPS were set to pump for 90 mins and typically filtered ~2000 litres, except at one station where the biomass had a high concentration and a 60 minute pump time was chosen.

10 deployments in total.

Total approximate volume of water filtered was 20,000 litres per SAPS

#### <sup>234</sup>Thorium

Aim: In order to convert a <sup>234</sup>Th number into a carbon number, and hence the downward flux of carbon, it is necessary to measure the particulate carbon to particulate thorium ratio – C:Th. This is the prime purpose of the thorium SAPS.

Each time a thorium profile was taken, the SAPS were deployed

The filter we put in the SAPS was 52µm nylon monofilament screen. 52µm was chosen because particles above this size are considered to be the sinking (and therefore exporting) particles.

Particles collected were split for <sup>234</sup>Th, POC/N, biogenic silica and chlorophyll.

#### Problems/suggestions

Frequently saw flecks of yellow paint in the sample, from the yellow painted shackles. Solution: stripped paint off shackles but ultimately use stainless shackles.

<sup>234</sup>Th SAPS 2 – frit and mesh not loaded in the correct orientation into the filter housing. Therefore the sample volume will not be reliable, but a sample was still taken. Suggested action: request a split from the iron SAPS for POC/N analysis and then back calculate a volume filtered for the thorium SAPS.

#### Iron

Aim: is to collect particles at the base of the mixed layer in order to measure Fe and C export then combine with Th:C (see above) to get an integrated flux of Fe from the upper ocean.

The filter we put in the SAPS was also a 52\_μm nylon mesh. Each of them has been pre-acid washed and pre-weighted at the University of Cape Town just before leaving on the cruise.

Immediately after collection, the excess of water in the housing was drawn off under vacuum in a flow laminar hood. The swimmers (copepods, jellyfish...) were taken out and placed in vials, then the filter was immediately put in a freezer at -20°C, together with the swimmers sample.

Fe and C measurements will be done at SOC, and then combined with Th:C data from samples in exactly the same way. The intention is to extend the range of elements from Fe alone and to look at series of other important elements, like P.

As anticipated, there were significant variations in amount of material collected reflecting the ambient biomass at each station sampled.

**Table 9.2 SAPS deployments on D285**

Station #	Station name	Day	Depth(m)	Pumping Time (hrs)	234-Thorium	Iron
					Volume Filtered (L)	Volume Filtered (L)
15492	M1	09/11/2004	200	1H30min	1980.1	1863.9
15495	M3	13/11/2004	225	1H30 min	2048.6	1933.8
15498	M3	18/11/2004	200	1H	1494.2	1501.8
15503	M2	19/11/2004	150	1H30 min	2085.1	2016.8
15512	M6	22/11/2004	175	1H30 min	2117.5	2052.8
15517	M3	25/11/2004	200	1H30 min	2094.5	1989.7
15523	M7	27/11/2004	150	1H30 min	2039.8	1939.6
15533	M8E	30/11/2004	150	1H30 min	2059.6	1972
15539	M8W	02/12/2004	150	1H30 min	2006.9	1842.1
15542	M9	09/11/2004	120	1H30 min	2015.4	1719.1

**Table 9.3 SAPS deployments on D286**

Station #	Station name	Day	Depth(m)	Pumping Time (hrs)	234-Thorium	Iron
					Volume Filtered (L)	Volume Filtered (L)
15554	M9	19/12/2004	120	1H30 min	2071.8	1851.5
15560	M10	20/12/2004	110	1H30 min	2016.0	1817.0
15573	M3	23/12/2004	180	1H30 min	2068.0	1845.0
15580	M5	27/12/2004	125	1H30 min	1310.0	1001.0
15590	M3	31/12/2004	100	1H30 min	1859.0	1909.0
15595	M6	03/01/2005	120	1H30 min	1802.0	1878.0
15604	M2	06/01/2005	160	1H30 min	1933.0	1653.0
15613	M3	09/01/2005	80	1H30 min	1627.5	1492.0
15621	M3	10/01/2005	80	1H30 min	1571.2	1492.3
15627	M3	12/01/2005	80	1H30 min	1758.9	2031.3

Problems/suggestions

To avoid any contamination while SAPS was on deck, a plastic bag was wrapped around the SAPS until deployment, and replaced immediately after recovery.

The Fe SAPS was placed above the Th SAPS to avoid contamination.

A weight was placed under the two SAPS to maintain them as vertical as possible in the water column.

**9.4 SAPS for ‘Proxy Calibration’ Study****Hélène Planquette**

SAPS were also used to collect particulate material from the upper water column for Dr. Rachel Mills (NOC) and Dr. Richard Pancost (University of Bristol) as a part of their proxy calibration study. The aim was therefore to collect particles at the depth of the chlorophyll maximum. The depth at which the SAPS were deployed was determined on a case-by-case basis. Parameters we used to determine this depth were water temperature, fluorescence and transmission. In total, 3 deployments were made during D286 at deployment depths ranging from 70 to 225m (see Table 1). SAPS were set to pump for 60 minutes and typically filtered ~500 litres.

**Table 9.3 SAPS for proxy calibration, blue (Pancost), yellow (Mills)**

Station #	Date (Julian day)	Name	Depth (m)	Volume filtered (L)
15579	361	M5	70	531
	361	M5	70	535
15598	4	M6	70	440
	4	M6	70	673
15620	11	M3	20	333
	11	M3	20	725



Fig. 9.1 SAPS filters from M3 15620 left: Nucleopore filter, right: GF/F filter

The SAPS filter for Pancost consisted of two 293  $\mu\text{m}$  diameter ashed GF/F filters, foiled in pairs. Two stacked GF/F filters were used to give greater structural strength to the filters and represent a nominal pore-size of 0.7  $\mu\text{m}$ . They were placed carefully with tweezers rinsed in methanol. SAPS filters for Mills were 1  $\mu\text{m}$  Nucleopore filters, placed in the SAPS filter holder under a laminar flow hood. Immediately after recovery of the SAPS pumps, excess water in the housing was drawn off under vacuum in laminar a flow hood. The filters for Mills were immediately rinsed with MQ water to remove the sea-salts. Filters were stored in a  $-20^{\circ}\text{C}$  freezer. They will be air-freighted back to University of Bristol and SOC.

As anticipated, there was a significant variability in the amount of material collected, reflecting the variable biomass at each station sampled.

The Nucleopore filters proved to be very difficult to handle, especially in a laminar flow hood, and were often found dislodged after filtration. It is recommended that during any future deployments the Nucleopore filters are supported on a matrix such as Nitex screen.