7. Iron Studies in the Crozet Region

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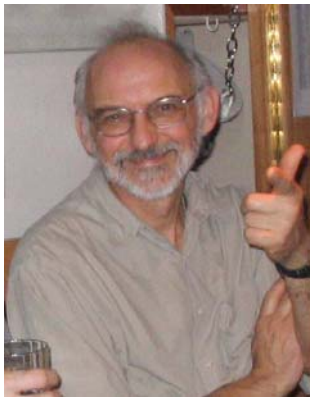

7.1 Dissolved iron

Main objectives

- To map changes in total dissolved Fe around the Crozet islands in relation to other key parameters including macronutrients, chlorophyll and phytoplankton species, in order to better understand the role of Fe in initiating and maintaining the bloom.
- To determine the vertical distribution of Fe at key stations around the islands in order to identify possible sources of upwelling Fe and the iron content of water masses.

The sampling objectives were to collect surface samples using the trace metal clean fish system and to collect samples from the vertical water column using the modified OTE bottles on the Titanium CTD-rosette system (UKORS).

Analytical Equipment

The Fe analyser system

The system is based on pre-concentration of Fe (III) and (II) from seawater onto an 8-hydroxyquinoline column, which is then subsequently eluted and mixed with a buffered luminol stream in the presence of hydrogen peroxide. The chemistry is carried out in a continuous flow system. The reaction leads to the production of light in the blue part of the spectrum, which is measured by a highly sensitive photo-multiplier tube [PMT], and the light emitted is directly related to the Fe in the original sample. Control of the flow system and data collection is done through a LabView programme, and NI DAQ and control cards.

The system had performed well at SOC immediately before D285 in analysing samples collected on recent cruises. However on D285 there was in initial major problem on the ship when on leaving Cape Town it was found impossible for the LabView programme to read the data stream from the PMT correctly and a variable high voltage was noted. A variety of time consuming tests were performed and even a chart recorder was rigged up to the system to monitor data. A solution was found by Robin Pascal, who re-grounded the channel 8 to another ground in the break out box. When this was done the system recognised the output from the instrument and the system worked as in the shore laboratory.

By the end of D285 another major problem occurred: The instrument showed poor sensitivity and there appeared to be random contamination of some samples. Despite new luminol solution

and replacement of most other solutions, no clear improvement was observed and the sensitivity remained poor. On the return to Crozet during D286, part of the system was rebuilt (new column, tubes, acid wash, fresh peroxide, heater temperature checking) to try to rectify the instruments problems. Several samples collected during the first leg were then analysed but they all still showed a high degree of contamination. To overcome this problem, an acid wash of the entire system was performed and a new batch of reagents was prepared.

Several vertical profiles (#15568, #15569 & #15572) were analysed during D286 but these results must be viewed with caution considering the number of problems encountered. They will be re-analysed back at SOC to ascertain any variations in concentration. A major problem observed later on was an inconsistent response of the analyser. For example, when the same solution was re-analysed, the peak heights differed and each time, the calibration failed. Thus, despite all the work done on the instrument, no improvement was observed and causes of the problems remain unclear. Work back at SOC post-cruise will involve re-evaluation of this system in comparison with an Fe analyser system recently set up at SOC by Dr Eric Achterberg.

Electrochemistry equipment

This system is used for on-board measurements of Fe-organic complexation. This data can be used with total Fe data to model the ligand concentrations, the different class of ligand (L1, L2), the conditional stability constants of these different ligand classes, and Fe(III)_ (soluble inorganic Fe(III) hydrolysis species). The instrumentation used consists of a PAR303A hanging mercury drop electrode connected to an Ecochemie 303 Interface and an Ecochemie μAutolab 3 voltammeter, the system was run using GPES software. During D286 major problems were encountered with the system. No signal was achieved due to a break in the mercury contact somewhere in the valve body or capillary. Despite numerous changes of capillary and cleaning of the valve body no signal was detected. The two 303A stands used had previously been serviced by Ametek before being packed for Crozex. Ametek will be contacted upon return to SOC to ascertain the reasons for the equipment not working in order to rectify them for analysis of samples returned to SOC. See section on Fe speciation studies for samples collected and future work.

Sampling Rationale

Underway TMS

During D285 a total of 210 surface samples were collected during the cruise. Water was pumped up from the clean fish (Fig. 7.1) at a depth of ~6m and into the clean container where it was withdrawn at the manifold either un-filtered or through a 0.2 μm filter cartridge.

Fig. 7.1 Underway Trace Metal Sampling (TMS) fish

Underway surface samples were collected during D285 (Fig. 7.2) on Crozex in order to provide a broad range of samples across the region of interest. Some problems were encountered:

The measured high Fe on passing between La Possession and Ile de l'Est, may be correct but could also be due to the potential contamination source noted by Mike Lucas. On this section samples

were collected with both fire hose (for Radium) and underway fish. When the fire hose was on, excess water for the pump is directed through hawsers at the bow of ship, and this iron laden water is discharged into the water surrounding the ship. There is clear potential for some of this water to be collected by the Fe fish. During earlier underway sampling at full speed, contamination was not overtly evident, but passage between the islands was at half speed. It was

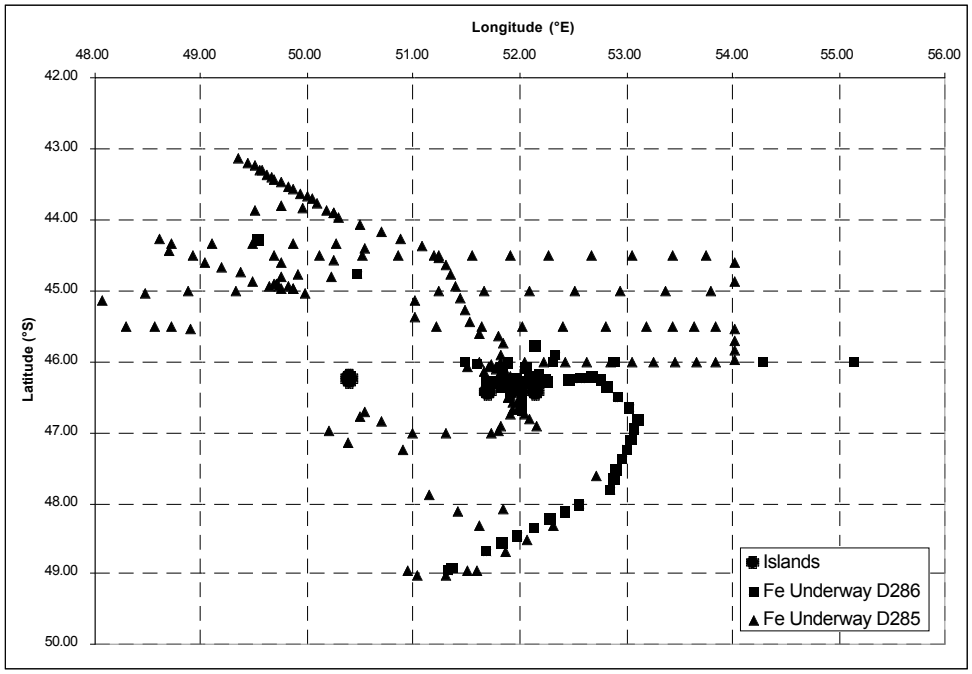

Fig. 7.2 Underway samples collected during Crozex cruises using the TMS Fish

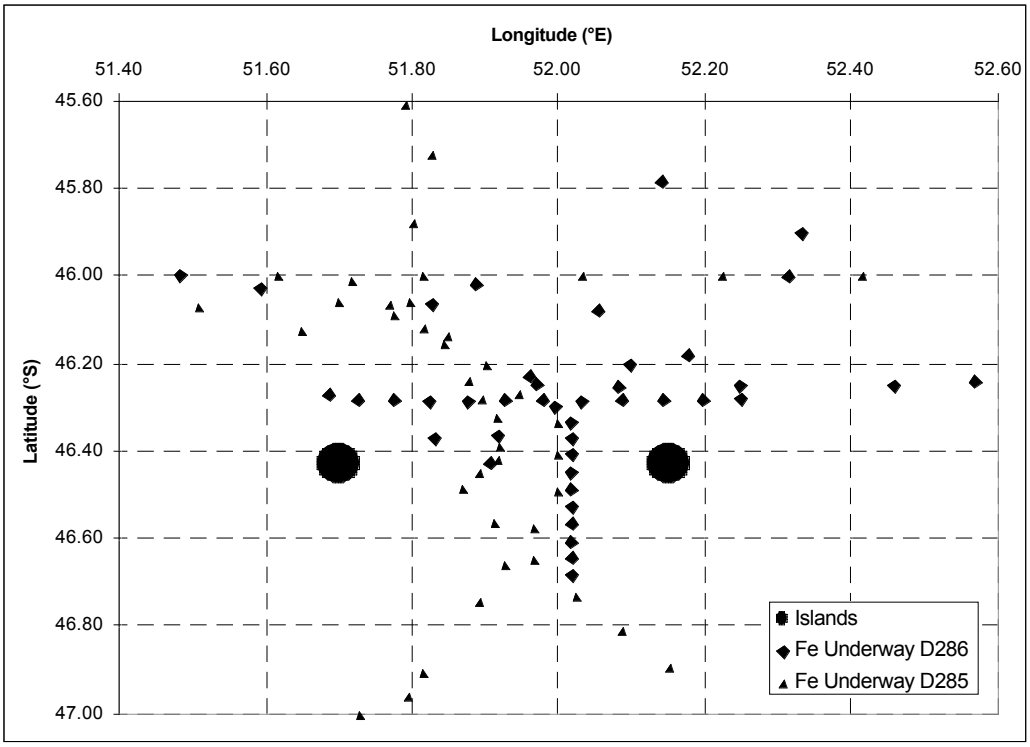

Fig. 7.3 Underway samples collected during Crozex cruises using the TMS Fish close to the Islands (Ile de La Possession and Ile de l'Est)

intended to resample on heading north between the islands later but at this time it seems the fish samples was also contaminated/non operational.

South of the islands in "HNLC" expected waters, a contamination problem was identified by the analyser (see below). It took about 3 days to resolve this problem and by this time the ship was back to the north of islands, and so there is limited data to south.

During D286 a total of 75 surface samples (Fig. 7.2) were collected during the cruise in order to improve the range of samples across the region, and to fill the gaps due to a lack of samples or contamination during D285. During D285, the samples collected on the passage between Ile de La Possession and Ile de l'Est and south of the islands shown to be contaminated. Therefore, a particular effort during D286 was made to get good samples at these locations (Fig. 7.3). Some further problems were encountered with the fish (pump). For details, see later report on that instrument.

Titanium CTD rosette system

During D285 a total of 11 Ti CTD stations were occupied (Table 7.1) and samples for dissolved iron collected. These samples were filtered through acid washed 0.2 µm polycarbonate filters housed in Teflon filtration units. Samples were collected in 1 litre and 0.5 litre trace metal cleaned LDPE bottles. Initially the samples were acidified with HCl (1ml per 1L – 6M). Analyses showed that this may have been a large contribution to the contamination. This corresponds to a total of 214 individual samples collected, and includes samples for other studies on Rare Earth Elements – REE (Section 4.7). Analysed vertical profiles follow the trends reported in the literature, although perhaps a little higher than given in some recent information, this may be however due to the problems encountered with the Fe analyser. In addition to giving Fe values for information on deep water sources, the surface data will provide information on water column Fe inventories.

Table 7.1 Titanium CTD stations occupied during D285

(Samples from stations in blue were measured on board ship. Samples in red are contaminated)

Station #	Name	Depth of cast (m)
15486	Test station	1000
15491	M1	~3100
15496	M3	2330
15502	M2	3842
15511	M6	4217
15516	M3	500
15524	M7	500
15526	M7	2722
15534	M8E	1000
15537	M8W	2770
15543	M9	2870

During D286 a total of 13 Ti CTD stations were occupied during the cruise. Samples were collected for dissolved iron (0.2 μm), Fe speciation studies and rare earth element studies. This corresponds to a total of 179 individual samples collected for dissolved iron, and includes 55 samples for speciation work (see later section). 26 samples were collected for rare earth elements (see separate section). Vertical profiles could not be analysed properly because of the failure of the analyser. All these samples were stored carefully in clean acid washed LDPE (dissolved iron) and Teflon (speciation work) bottles for analysis back to SOC. Samples for dissolved iron analysis are usually acidified prior to storage and measurements to avoid any reactions due to the biology. However, none of the samples were acidified due to too many problems of contamination by the acid itself during D285. A decision was therefore made to ship all the samples back to SOC so that they can be analysed there using several methods in order to establish accurate Fe concentrations. Dissolved iron will be analysed at SOC using the Fe analyser system of Eric Achterberg, multi-collector isotope dilution inductively coupled plasma mass spectrometry after $Mg(OH)_2$ coprecipitation and using cathodic stripping voltammetry after microwave digestion. This will enable accurate measurements to be made free of contamination worries and also it will give the opportunity to undertake a laboratory inter-comparison of Fe analytical techniques.

Table 7.2 Titanium CTD stations occupied during D286

(BUS refers to the stations done in Baie Americaine, Ile de la Possession)

Station #	Station Name	Depth of cast (m)	Sampling depths (m)
15552	M9	3200	5;15;35;75;125;200;500;1000;1500;2000; 2500;3200
15563	M10	2897	5;15;35;75;125;200;500;1000;1500;2000; 2500;2897
15567	BUS	80	5;25;50;80
15568	BUS	376	5;25;50;100;200;300;376
15569	BUS	1470	5;25;50;100;300;750;1000;1250;1470
15572	BUS	175	5;25;35;75;175
15581	M5	4220	5;40;60;100;170;300;500;1000;1250; 2500;3000;4000;4220
15592	M3	200	5;25;55;100;200
15598	M6	4168	5;10;20;40;60;80;100;160;225;400;750; 1000;1500;2000;3000;4000;4168
15605	M2	3810	10;50;100;160;300;500;750;1000;1500; 2000;3000;3500;3810
15612	M3	500	10;60;100;160;500
15622	M3	2288	5;20;80;150;300;500;750;1000;1250; 1500;2000;2288
15629	M3	500	5;8;12;20;35;55;80;100;150;300;500

Sample collected with the Pole Sampler

During D285, in order to check the surface water concentration data obtained by the fish system, a separate sample was collected using a clean bottle on the end of a pole on 29 November 2004. The concept is that the pole can be deployed away from the ship and thus the sample can be collected in un-contaminated water. However when analyzed both the fish sample taken at the same time and the pole sample appeared to be contaminated, suggesting a halo of iron contamination had developed around the vessel whilst on station. Some earlier data had also suggested the ship as a contamination source on station.

Fe Speciation Studies

Background – Although abundant in the earth's crust iron (Fe) is relatively insoluble in oxygenated sea water resulting in concentrations that are known to limit phytoplankton growth and nitrogen fixation rates over large areas of the ocean. The physicochemical speciation of Fe in seawater determines its bioavailability and the primary productivity of the phytoplankton thereby directly linking the biogeochemistry of iron and carbon (C) in the sea. Our knowledge of Fe speciation in seawater, however, is severely limited due to a lack of measurements of Fe concentrations and its degree of organic complexation in seawater. The few existing electrochemical measurements of Fe speciation demonstrate that greater than 99% of the operationally defined "dissolved" Fe that passes through a 0.4 micron filter is strongly bound to organic ligands of presumed biological origin. These ligands were thought to be of low molecular weight, slow to adsorb onto particulate surfaces and have long oceanic residence times. However, recent studies using microfiltration and low level Fe analysis by HR-ICP-MS indicate that soluble (<0.02 microns molecular diameter) Fe and organic ligand concentrations are much lower than previously determined in the "dissolved" (<0.4 micron) fraction. A significant fraction of "dissolved" Fe and Fe binding ligands may actually exist in the colloidal size range. These results suggest that "dissolved" Fe may be less bioavailable to phytoplankton than was previously thought and that colloidal aggregation may be an important Fe removal process in the ocean.

This program of research aims to investigate the distribution and importance of the soluble and dissolved Fe(III) fraction in the water column and close to the sediments of the Crozet Island region. Knowledge of the size distribution of Fe species and the strength of its organic complexes is of paramount importance in oceanography in order to incorporate Fe into biogeochemical models of the oceanic C cycle. One of the major goals is to elucidate the size fraction and binding strength of these exuded ligands which can further our knowledge as to the bioavailabilty of Fe in HNLC zones.

Methodology – Seawater was collected using the TiCTD at stations and depths of major interest (Table 7.3). After filtration through the 0.2 micron filters and collection in Teflon bottles the water was further filtered through Whatman Anodisc 0.02 micron filters using a dedicated separate Teflon filtration unit (Fig. 8). The 0.02 micron fraction was stored n 250 ml LDPE bottles for further analysis at SOC. Due to the unavailability of the CSV equipment, 19 0.2 micron fractions in Teflon bottles were frozen for subsequent analysis at SOC. Previous studies have shown that immediate freezing of the samples retains the integrity of the sample for future speciation studies.Analysis will be undertaken at SOC using the technique of CLE-ACSV

Fig. 8 Teflon filtration rig

(Competitive ligand exchange – adsorptive cathodic stripping voltammetry) with the added ligand TAC. Complexing capacity titrations will be undertaken on the samples to determine the Fe-TAC response over a series of increasing Fe concentrations (0.2 to 5 nM) . Total dissolved Fe in the two fractions will be measured in the laboratory at Southampton Oceanography Centre. The seawater will be subjected to UV irradiation and analysed using CSV with DHN as the added ligand. Total Fe values will also be determined using high-resolution isotope dilution inductively coupled plasma mass spectrometry after $Mg(OH)_2$ coprecipitation. After the total values have been measured the numbers combined with the complexing capacity titrations can then be used to yield the ligand concentrations, the different class of ligand, the conditional stability constants of these different ligand classes, and Fe(III)_ (soluble inorganic Fe(III) hydrolysis species).

Table 7.3 Titanium CTD stations sampled for Fe speciation studies during D286

(Frozen Teflon samples in bold, 0.02 μm samples in italics)

Station #	Station Name	Depth of cast (m)	Sampling depths (m)
15563	M10	2897	*5;15;35;75;125;200;500;1000;1500; 2000;2500;2897*
15581	M5	4220	*5;40;100;170;500;1000;1250;2500;4000;42*
15598	M6	4168	**5; 10; 20; 60;100;400;1000;2000;3000; 4000;4168**
15605	M2	3810	*10;50;100;160;500;1000;2000;3000;3500;3* *0*
15622	M3	2288	***5;20;80;150;500;1000;1500;2288***

7.2 Particulate iron

Pelagra Sediment Trap Samples

An important component of the surface water mass balance of Fe is its removal through association with particles that are transported into deeper waters. A direct way to measure this flux is with sediment traps. Each Lagrangian trap can be programmed to stay at a set depth in the water column for a set period of time, and each of the 4 X 0.1 meter squared cones should in theory collect similar material. One trap cup for each deployment was designated for Fe work and did not contain any preservative. During D285 there were 6 deployments. PE1 was lost, and for PE6 no material was collected because the closing mechanism did not work correctly. For PE6, a large deposition event was intercepted. As the Fe cup was found to be empty, a sub-sample of the 2% formalin preserved sample together with a sub-sample of the formalin solution used in the trap cup, was taken and frozen for later analysis at SOC

During D286 there were 6 deployments, but only 3 were kept for iron work.

Particles and overlying solution in the cups were separated onboard the ship by filtration through pre-weighed filters (20 mL on ashed GF/F filters and 500 mL on 0.2 μm Nucleopore membrane filters). Iron in both particles and dissolved phase will be determined back at SOC. Measurement of Fe in both phases is necessary as some loss of Fe into the dissolved phase may occur during deployment. One problem noted with the trap samples was the frequent collection of paint particles with the biogenic material present. This was partly relieved by shrouding the hook

weight on the crane used during deployment and retrieval, which appeared to be an important source of these red paint particles. Black paint from the trap lifting frame was also removed at the beginning of D286 by Ian Salter. See Pelagra section for more information on the deployments.

Integrated Fe fluxes from the upper ocean using Stand Alone Pump System (SAPS)

The aim was to collect particles sinking from the biologically productive mixed layer of the water column in order to measure C and Fe export from the upper ocean. When combined with ^{234}Th:C ratio(see section in the report on ^{234}Th), an integrated flux of Fe from the upper ocean can be calculated. 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. We aimed to place 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. Therefore, SAPS were deployed below the thermal mixed layer, ie below the chlorophyll maximum and below the point of increasing transmission corresponding to decreasing chlorophyll concentrations. We then gave ourselves around 20m margin of error below these features.

In total, 20 deployments were made at deployment depths ranging from 70 to 225m (see Tables 7.4 and 7.5). SAPS were set to pump for 90 minutes except at one station where the biomass had a high concentration and a 60 minute pump time was chosen (D285, station 15499#2) and typically filtered ~2000 litres.

Table 7.4 sampling details for SAPS during D285

Station #	Station name	Depth (m)	Volume filtered (L)
15492#2	M4-1	200	1863.9
15495#2	M3	225	1933
15499#2	M3	155	1501.8
15503#2	M2	150	2017.3
15511#1	M6	200	2052.8
15517#2	M3	200	1989.7
15524#1	M7	150	1939.6
15533#1	M8E	200	1972
15539#2	M8W	150	1842.1
15543#2	M9	120	1719.1

The filter put in the SAPS was a 52 μm nylon mesh monofilament screen chosen because particles above this size are considered to be the sinking and therefore exporting carbon. Each filter was acid washed and pre-weighted at the University of Cape Town (UCT) just before leaving on cruise D285. Immediately after recovery of the SAPS pumps, excess water in the housing was drawn off under vacuum in a flow laminar hood. The swimmers (i.e copepods, jellyfish etc) were removed and placed in vials, then the filter was immediately put in a freezer at –20°C, together with the sample of swimmers.

Table 7.5 sampling details for SAPS during D286

Station #	Station name	Depth (m)	Volume filtered (L)
15554	M9	120	1861
15560	M10	110	1817
15573/2	M3	180	1945
15580	M5	125	1001
15591	M3	100	1909
15595	M6	120	1878
15604	M2	160	1653
15613	M3	80	1492
15620	M3	80	1493
15628	M3	80	2031

Fe and C measurements on the particulate material will be carried out at SOC, and then combined with ^{234}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, such as P.

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

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

7.3 Shore Sampling

The major hypothesis of the Crozex programme is that phytoplankton productivity in the seas surrounding Crozet is enhanced because of natural Fe fertilisation of surface waters. Following this, a key point to ask is to identify the source of Fe. Two possibilities exist which are not mutually exclusive. One is that as deep water rises towards the surface as it flows northwards over the Crozet plateau, it brings Fe-enriched water to the surface. The other is that freshwater run-off from the islands introduces Fe and perhaps silicate and other nutrients into the near-shore surface waters. During D286, a sampling expedition was undertaken the Ile de la Possession on the 8th of January. This was to collect sediment and water samples both in fresh water areas and coastal input areas. See separate section for details and also radium section.

7.4 Report on facilities and equipment used in Fe work

Clean container laboratory

Overall the container lab worked well, and provided a high quality environment for the taxing trace metal work being undertaken in CROZEX. One problem noted was with the water sample bottle rack in the entrance area where the coating on the frame had begun to flake away and the iron

corrosion exposed become a significant contamination concern. Richie Phipps provided a bolt on plastic inset to isolate the bottles from the corrosion just at the end of D285.

Underway clean Fish sampling system

At the end of the cruise prior to D285, the fish system was in a bad state of repair. The bottom cover and weight had be lost, the original LDPE tubing had been replaced by reinforced PVC tubing taped to the exterior of the faring, and the intake tube had been broken. Richie Phipps undertook a major rebuild and rethink of the operation of the fish system. The bottom weight was replaced and a spare bottom cover fitted. A new length of LDPE tube was fitted, and crucially a line was fitted to the end of the fish and secured on the aft port quarter to prevent the fish rotating (which had apparently caused much of the damage to the original system) when on station. These modifications proved very successful and the fish proved to tow well at about 2 m depth and at about 8 m from the midships of the vessel. During D285, a series of mechanical problems were encountered with the fish operation, and then overcome:

1) The bolts holding on the end housing of the pneumatically operated pump loosened, allowing air leakage and stopping of the pump. Careful tightening solved this problem (caution needed as both parts of pump are plastic).
2) The independent compressed air supply for the fish pump failed. This turned out to be an overheating problem related to the level of the lubrication oil being too low. Once replaced, the compressor started again and once settled down performed satisfactorily.
3) The fish stopped pumping and as the compressed air supply was working the pump itself was stripped down. The problem was tracked to a stuck ball valve at the inboard side of the pump. The pump was reassembled and then functioned correctly.
4) A major problem arose when south o f the Crozet islands when the underway samples began to give very high values. The problem was identified as being two breaks in the tube system. The tube at the junction with the fish had sheared off and further up the faring the tube had parted in a second position where one of the faring location clamps had worn through the tubing. The fish faring and tubing had to be completely removed and refitted, right back to the winch. Initially there was a problem with getting the fish to self prime at this point.

However the problem was tracked to a split tube that was allowing air into the system. On refitting the tubing, the fish system worked correctly. A minor problem occurred when a length of tubing behind the Forecastle level container rubbed on a box and eventually wore through, leading to a substantial leak. This leaking section was cut out, the tube rejoined and the length of tubing running aft re-secured. A similar problem arose with the tubing on the after deck adjacent to the clean container (6 Dec 2004), where the pulsing action of the pump led to rubbing of a length of tube against the deck and eventually the wall of the tube was completely worn through and leaked. During D286, only one major mechanical problem was encountered with the fish operation. The fish stopped pumping on the night of the 11th of January. The fish was then brought back on the ship. The problem was identified as being one break in the tube system close to the fish itself. The tubing had to be completely removed and refitted. Once the tubing had been refitted, the fish system worked correctly. Overall the fish system worked well considering the frequently rough weather encountered, in providing a pulsed stream of clean water at a flow rate of about 5L/min. The efforts of the UKORS staff (Richie Phipps –D285; Ian Waddington, Emma Northrop and Alan Davies – D286) in keeping this system operational, are much appreciated.