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12 MAY 1983  
(WORMLEY)

RRS DISCOVERY

CRUISE 129

29 MAY - 22 JUNE 1982

I.O.S.

GEOCHEMICAL SAMPLING IN THE  
TROPICAL AND SUBTROPICAL EASTERN  
ATLANTIC

CRUISE REPORT NO 138

1982

NATURAL ENVIRONMENT  
INSTITUTE OF  
OCEANOGRAPHIC  
SCIENCES  
RESEARCH COUNCIL

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INSTITUTE OF OCEANOGRAPHIC SCIENCES  
WORMLEY

R.R.S. DISCOVERY

Cruise 129

29 May - 22 June 1982

Geochemical sampling in the  
tropical and subtropical eastern  
Atlantic

Principal Scientist

T.R.S. Wilson

I.O.S. Cruise Report No. 138

1982

*The work described in this report has, in part, been carried out under contract for the Department of the Environment as part of its radioactive waste management programme. The results will be used in the formulation of Government policy, but at this stage they do not necessarily represent that policy.*

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## ITINERARY

Depart Abidjan 29 May 1982

Arrive Tenerife 22 June 1982

## SCIENTIFIC PERSONNEL

Miss J. Clancy	Southampton University
Mrs. S. Colley	I.O.S.
B. Elloway	R.V.S.
M. Greaves	Leeds University
N. Hill	I.O.S.
D.J. Hydes	I.O.S.
R. Kirpalani	I.O.S.
B.G. Knowles	I.O.S.
G.A. Lake	I.O.S.
V.A. Lawford	I.O.S.
A. Lewis	R.V.S.
M. Palmer	Leeds University
P. Statham	Southampton University
Mrs. H.E. Sutherland	I.O.S.
J. Thomson	I.O.S.
R.F. Wallace	I.O.S.
T.R.S. Wilson	I.O.S. (Principal Scientist)

## SHIP'S OFFICERS

S.D. Mayl	Master
E.M. Bowen	Chief Officer
J.T. Morse	2nd Officer
T.J. Boulton	3rd Officer
A.E. Coombes	Chief Engineer
P.J. Byrne	2nd Engineer
I. McGill	Extra 2nd Engineer
R. Cotter	3rd Engineer
K.T. Sullivan	5th Engineer
F.P. Sharpe	Electrical Engineer

B.A. Smith  
R. Cridland  
P. Taylor

2nd Electrical Engineer  
Purser/Catering Officer  
Radio Officer

## OBJECTIVES

1. To investigate early diagenetic processes, especially denitrification, in sediment profiles from the equatorial Atlantic high productivity zone obtained by coring.
2. To obtain carbonate saturation data from the pore waters of similar geochemical provenance but differing depth.
3. To sample sediments and pore waters in the CV2 and GME areas as part of the international high level nuclear waste disposal evaluation programme, with special emphasis on redox-related phenomena.
4. To continue in situ filtration tests in the water column, and to obtain preliminary data using this equipment.
5. To conduct a programme of water column sampling in conjunction with the in situ filtration experiments, especially concentrating on manganese distribution.

## NARRATIVE

The scientific party was embarked by 2000 Z 26 May. On the following day the major items of scientific equipment were broken out, positioned and secured for sea in order to be in a position to sail that evening. In the event, however, problems with the ship's bilge pumps, and with the air conditioning water intakes, prevented sailing until 1000 Z on 29 May, so that it was possible to perform most of the detailed preliminary preparation of equipment before sailing.

The P.E.S. transducer fish was deployed at 1100 Z, 30 May. Scientific watches started at 0000 h/31 May. The shakedown station was reached at 1230 Z. The traverse gear on the traction winch gave problems, so that an average speed of 0.3 m sec was all that could be obtained during the first lowering, for a Kasten core. During the recovery phase much better speeds were obtained, averaging 0.9 m sec<sup>-1</sup>. The forward electric winch was used for the next operation a Niskin bottle cast. As this winch had not been used for some months a careful watch was maintained during the early deployment operations. Problems were experienced with the wire binding in the accumulator and fairlead, and loose turns were thrown on the drum. Prompt action by the winchroom watch prevented serious difficulties, and the problem was rectified. Further deployments (see Table 1) on the midships and traction winches at this station proceeded without incident.

On the last drop, a boxcore, a sampler pretrip was detected at 5020 m wire out, using the special Near Bottom Echo Sounder (N.B.E.S.), and the sampler was recovered without a core.

Between stations a modification was fitted to the box core no-load release, designed to prevent pre-trips by means of a locking device opened at depth by a shear-pin assembly. On arrival at the next station position a search of some eight hours was necessary to locate a bottom flat enough to core. Successful Kasten and Box cores and water column (CTD) samples were recovered: the sediment was very coarse-grained and did not exhibit the reduction at depth reported by previous researchers sampling near this site. The pore water sampler (PWS) suffered a voltage regulator failure and did not sample: because of the core observations, it was decided not to repeat this deployment at this site. The in situ water column filtration unit (F.I.D.O.) experienced some flow blockage problems which were overcome. CTD profiles exhibited a most complex and impressive stepped structure at this station.

At the next station, reached at 0054 Z 5 June, it was decided to sample as close as possible to the position occupied by previous workers (Froelich et al, 1979). Fortunately, a suitable site for coring was located at the expected position, and a full suite of bottom and water column samples was obtained, with the exception of the in situ pore water sampler, which failed to sample, apparently because of problems related to the voltage regulator failure at the previous station. After careful study the cause of these problems was located and rectified, and the problem did not reoccur at subsequent stations.

Time constraints dictated that this should be the last station of the equatorial sequence, the projected deep station in the Romanch fracture zone being abandoned. Course was set for the Cape Verde site (CV2). During this passage, 2 water column stations were worked, one with FIDO sampling, and Neptune visited the ship to 'welcome' those who had crossed the equator for the first time.

On arrival at CV2 (1930 Z, 12 June) Kasten and FIDO deployments were made. Excellent weather conditions then permitted a zodiac deployment to study near-surface trace-metal distributions and possible ship-source contamination effects. The station was completed with three box core and two PWS deployments, together with deep FIDO and CTD samples. During this sequence the most serious problem experienced with the traction winch system during the cruise occurred. The final guide-pulley on the traverse gear seized with about 5000 m of wire out, and it was necessary to stop-off the warp inboard of the traction unit so as to remove



and repair the pulley bearings. This was successfully and rapidly accomplished by I.O.S. and ship's engineers working together, and the scientific programme proceeded without serious interruption.

Weather conditions during the final section of the cruise improved even further, with the wind falling to a flat calm on the final station east of Great Meteor seamount (GME, 0130 Z 18 June). This enabled a full series of samples to be taken, including two Kasten cores two box cores and two sets of P.W.S. samples. A further zodiac deployment was also made. The final station was forsaken at 0500 Z on 20 June. Scientific watches ended at 2400 Z on that date. A direct passage to Tenerife was broken only by a failure of the ship's propulsion system later that morning, which was rectified after 4 hours. The P.E.S. fish was recovered during this period. Discovery reached Tenerife as scheduled at 0900 Z on 22 June.

#### REPORTS OF PROJECTS

#### SEDIMENT SAMPLING

There were requirements on this cruise for solid phase material from the sediment/water interface downwards for sediment characterisation and dating studies, for pore waters squeezed from core subsamples for augmentation of the in situ pore water device samples and for pore water REE content assay. The corers used were the I.O.S. 30 cm<sup>2</sup> box corer (to sample the near-surface sediments) and a Kasten gravity corer with 2m or 4m 15 cm<sup>2</sup> square section barrels (to sample to greater depth).

A standard I.O.S. 10kHz beacon modified to transmit a more powerful signal was used on all corer runs and markedly improved bottom return echoes. Problems with box corer pretrip on Cruise 125 caused the introduction of two additional features to box corer operations. One was a shear pin retractor which allowed the corer no-load release to operate only after the shear pin had failed: pins to shear at depths of 2900 m and 3500 m were available. This device also allowed the corer to be run out at greater speed to the shear depth. The second was a near-bottom echo sounder (NBES) incorporated into the main beacon unit which detected corer pretrip on descent: the NBES signal recorded on the P.E.S. indicated a large offset relative to the main pinger pulse if the corer pretripped and consequently changed its distance from the NBES.

Coring was undertaken at 5 stations, three in the equatorial region (10547, 10548 and 10549), one in the Cape Verde 2 area (10552) and one in the Great Meteor area (10554). The Kasten corer operated well and retrieved six 2 m (nominal) and one 4 m (nominal) cores with no failures. Five successful box cores were taken (at stations 10548, 10549, 10552 and two at 10554) with three failures due to pre-trip at depths greater than 4 km. All cores were sampled intensively for sediment (for later shore work up) and for pore waters. Nutrient data for the pore water were obtained aboard ship which revealed no major differences between the cores taken at individual stations, and good agreement with similar data from the in situ sampler.

H.E. Sutherland  
J. Thomson

#### SEDIMENT PORE WATER IN SITU SAMPLING

The Mk II I.O.S. In-situ Pore Water Sampler was deployed a total of 9 times at 6 stations on this cruise. The sampler functioned correctly on 6 lowerings. High sample yields were obtained - up to 86% of the theoretical maximum achievable. Determinations of silicate, phosphate, nitrate, oxygen, nitrogen, nitrogen/argon and total carbon dioxide in the samples were carried out on board ship.

Two failures which occurred early in the cruise were due to a fault in the electrical circuit. This was solved by Mr. T.P.J. Gwilliam, and the electrical system functioned perfectly for the rest of the cruise. The third failure was due to a contaminated valve in the hydraulic circuit. On two further deployments the samples were partly compromised by towing-over of the instrument while it was in the process of sampling on the sea bed. This is a problem for which a solution still has to be found.

N.C. Hill  
D.J. Hydes  
T.R.S. Wilson

#### HYDROGRAPHIC SAMPLING

##### Rosette Sampling

The majority of the water sampling was performed using a rosette sampler fitted with 10 teflon lined 2.5L Go-Flo bottles, deployed in conjunction with a CTD system. This unit functioned well throughout the cruise.

Because of the failure of the pressure operated opening device on several bottles, it was necessary to send these bottles down open. A total of 103 sea water samples were successfully taken; there were only 3 occasions when a bottle did not fire and close correctly. Shallow casts (1500 m) were made at all stations with deep sampling at stations 10548 and 10552. The water from the Go-Flos was routinely sub-sampled for nutrients, dissolved oxygen, salinity and dissolved aluminium (Wormley) and the remaining water was pressure filtered (using nitrogen from the onboard generator) directly from the bottles through 0.4µm Nuclepore membranes.

On stations where the large volume filtration sampler was to be deployed, the CTD was run to within 10 m of the bottom without sampling to provide the salinity and temperature information needed for filtration deployment planning.

Trace metals were complexed using a mixed dithiocarbamate reagent, and extracted into freon TF (total number of samples extracted = 79). The metals were back extracted from the organic phase under acid conditions, and stored in a dilute nitric acid solution ready for transport back to Southampton and subsequent graphite furnace atomic absorption analysis. The main elements of interest were Mn, Cd and Fe, but as the technique is capable of quantitative recovery of Co, Ni and Cu, the procedure was calibrated for these elements as well. At the last station a series of replicate samples were ultra-violet irradiated under acid conditions to bring any colloidal and organic forms into solution prior to being passed through the extraction procedure. At all other stations, sub-samples of filtered sea water were acidified and stored in acid leached polyethylene bottles ready for later processing at Southampton.

Nitrite was determined onboard in samples from the upper part of the water column at five stations. Further sub-samples for dissolved organic carbon analysis were taken at stations 10548 and 10552, where water from depths throughout the water column was available. After passing through pre-heated GF/F filters, samples were frozen and stored ready for subsequent analysis at Southampton.

At station 10548, 19 2L samples from depths throughout the water column were taken and stored after filtration (0.4 µm Nuclepore) and acidification ready for rare earth element analysis at Leeds.

#### Large Volume Sampling

At station 10548, 60L samples were taken at five depths using a 60L Go-Flo and 30L Ni kin bottles. These sea waters were filtered through 0.4 µm Nuclepore

membranes and acidified, ready for transport back to Leeds for Neodymium analysis.

#### Surface Sampling

A set of 17 surface samples was taken using the shipboard non-toxic sea water supply. After filtration and acidification the samples were stored for trace element analysis at Southampton. The same sampling scheme was used by Leeds to obtain five 60L surface samples for rare earth element analysis.

Surface samples were taken by hand from a zodiac inflatable, positioned some 1 km upwind of Discovery at stations 10552 and 10554. At each station a 60L sample (Leeds, rare earth elements) several 1L samples (Southampton, trace metals) and 250 ml samples (Wormley, aluminium) were taken. This should provide uncontaminated samples against which to compare surface water taken by other methods.

J. Clancy  
M. Greaves  
M. Palmer  
W.R. Simpson  
P. Statham

#### CORE SQUEEZING AND NUTRIENT ANALYSIS

136 core samples were squeezed ( 2°C) after subsampling under nitrogen in a glove box. Using the Pye Unicam Automated Chemistry System a total of 790 determinations (silicate (340) phosphate (273) nitrate (124) and nitrite (53) were performed on samples of water column sea water collected in water bottles and sediment pore waters obtained by in situ sampling and from squeezed sediment cores. Dissolved oxygen was determined in 117 water column samples by the Winkler titration method. Minor problems were encountered with the Pye system on this cruise but they were overcome, and all required analyses were complete before arrival at Tenerife.

S. Colley  
N.C. Hill  
D.J. Hydes

## DISSOLVED GAS ANALYSIS

A new method of dissolved gas analysis for in situ pore water samples was initiated on this cruise. This procedure gave oxygen and nitrogen values as before, but also provided a ratio of nitrogen to argon so that argon (presumed inert) could be used as an internal standard for the other atmospheric gases. After problems with the sampling procedure at earlier stations this analysis worked well, and useful data was obtained at the more northern sites.

As noted elsewhere, attempts to use micro electrodes to profile dissolved oxygen in cores were unsuccessful. However, in recompense, it proved possible to combine elements of the bacteriological procedures and the gas analysis system described above to give an entirely novel method for dissolved oxygen in core samples. By this means an estimate of the molecular oxygen level could be made using small samples from cores. It was shown that these results were comparable with the in situ sample values thus validating the procedure. The method does not give ratios to argon, as its sensitivity is too low, but is very suitable for redox system studies and should find wide application. Over 75 oxygen determinations were made using this method during Cruise 129.

J. Sørensen  
T.R.S. Wilson

## IN SITU LARGE VOLUME FILTRATION (FIDO)

Particle samples were collected at a number of stations using the in situ large volume filtration system. A summary depths, volumes and filtration time is to be found in Figure 2.

The difficulties encountered on Cruise 125 have largely been overcome. A new particle cell operated successfully as a continuous profiler to depths approaching 6000m. The redesigned filter stacks appear to prevent wash-off of sample during recovery. Real-time plotting was achieved of particle data, flow and battery voltage; data summaries, including flux estimated were also printed.

The major difficulty arose from electrical breakdown within General Oceanics plugs and sockets, which, although rated at 15 amps, were incapable of taking the 9 amp current supplied from the battery packs. On occasions the resulting damage caused spiking in the continuous sensors, loss of flow and loss of control of the instrument from the ship. Apart from this the only outstanding problem is with the timing of the water-bottles: this mechanism is being redesigned at

present.

On this cruise it was possible not only to use the C.T.D. data and transmissometer data to select sampling depths, but also to monitor the one second record of the first channel of the particle counter ( $\Sigma > 10\mu\text{m}$ ) and the full particle data sets (16 see record). In this way particle maxima and minimum were sampled throughout the water column to within 10m of the bottom.

T.J.P. Gwilliam  
R. Kirpalani  
V.A. Lawford  
W.R. Simpson

#### BACTERIOLOGY

Samples were recovered for denitrification activity assay at four stations, including cores with and without strong redox gradients. These were equilibrated with acetylene gas in order to block the biochemical denitrification pathway, and returned to Aarhus for the analysis of nitrous oxide content; this intermediate accumulates if denitrifiers are present.

Additionally, it had been hoped to measure oxygen profiles using micro-electrodes previously developed for studies in salt marsh environments. However, the sediments encountered on this cruise proved to contain a coarse fraction which prevented the electrodes from penetrating and caused fracture of electrodes. No useful measurements were obtained from this experiment. However, a modification of the bacteriological assay procedure was made which permitted direct measurement of oxygen in sediment samples: a considerable amount of information (see analytical section) was obtained using this procedure.

J. Sørensen

#### DECK MACHINERY

##### Aft Winch

The new aft traction winch system was used extensively on this cruise (over 100 hours total running), for deep cores and pore water sampling. A few problems were experienced, mainly with the traverse, but these caused little loss of scientific time. At the start of the cruise a new slew motor was fitted to the aft davit to increase the available torque, and the slip-ring assembly was repaired. Both these items worked well throughout the cruise.

### Forward Ring Main

Modifications were made on the system on this cruise to protect the gauges from surge pressures. These proved effective. The starboard winch, used for FIDO and CTD deployments, worked well throughout the cruise with little downtime, the major malfunction being a burst hydraulic line. No loss of scientific station time was incurred.

R.F. Wallace  
B.G. Knowles  
G.A. Lake  
V.A. Lawford

### SUMMARY

All the listed objectives were achieved, with the exception of the carbonate saturation study which was deleted through lack of time. The high level waste site GME (10554) was enhanced in priority at a late planning stage, after bad weather was encountered at this site on cruise 125. We were most fortunate to be able to achieve excellent sampling recovery at GME on this cruise. The direct comparison of the geochemically contrasting sites GME and CU2 (10552) was particularly rewarding, as it provided the first direct evidence that these sites embody strongly contrasting redox environments.

### ACKNOWLEDGEMENT

It is a particular pleasure to be able to record my thanks to the Master, Officers and crew of R.R.S. Discovery for their unstinting efforts in support of the scientific programme, without which none of the work recounted here would have been possible.

Some of the research described in this report has been carried out under contract for the Department of the Environment, as part of its radioactive waste management research programme. The results will be used in the formulation of Government policy, but at this stage they do not necessarily represent Government policy.

TABLE 1 - Summary of sampling operations Discovery Cruise 129

Station and series number		Date	Lat. deg	min	Long. deg	min	Operations	Time (G.M.T.)	Remarks
10547	1	31.V	00	13.3N	08	57.7W	KASTEN	1728	2m. 5100m
	2		00	08.9N	08	57.4W	NISKIN	2036	
	3		00	09.6N	08	57.0W	FIDO	2151	
	4	1.VI	00	10.6N	08	57.4W	P.W.S.	0140	5160m 75%
	5		00				BOX	0733	Pretrip at 5100m.
10548	1	2.VI	00	00.3N	13	24.7	CTD	1310	
	2						KASTEN	1511	Aborted - winch problem
	3		00	01.3N	13	22.2W	CTD	1735	
	4		00	01.8N	13	22.4W	KASTEN	2034	2m 3890m
	5		00	01.4N	13	21.0W	NISKIN	2335	
	6	3.VI	00	02.9N	13	19.0W	FIDO	0311	
	7		00	03.9N	13	17.9W	BOX	0500	47cm 3890m
	8		00	03.3N	13	16.5W	CTD	1104	
	9		00	02.7N	13	15.4W	P.W.S.	1550	Electronic malfunction
	10		00	02.4N	13	14.7W	FIDO	2105	
	11	4.VI	00	02.7N	13	14.0W	CTD	0048	
	12		00	02.9N	13	13.5W	NISKIN	0233	
	13		00	04.6N	13	11.8W	CTD	0751	
10549	1	5.VI	00	03.5S	16	09.7W	KASTEN	0300	2m. 3535m
	2		00	04.6S	16	09.5W	CTD	0542	
	3		00	03.3S	16	08.0W	P.W.S.	1019	Electronic malfunction
	4		00	04.5S	16	08.0W	FIDO	1434	
	5		00	02.9S	16	07.4W	BOX	1700	48cm 3046m
	6		00	01.9N	16	10.2W	KASTEN	2208	2m 3150m



10550	1	9.VI	09	59.9N	25	59.3W	FIDO	1138	
	2		10	00.4N	25	59.9W	CTD	1811	
	3		10	01.0N	26	00.8W	P.W.S.	2220	5180m 51%
	4		10	01.0N	26	00.8W	CTD	0128	
	5	? 10.VI	10	00.8N	26	00.6W	FIDO	0159	
<hr/>									
10551	1	11.VI	14	54.4N	27	56.5W	CTD	1018	
	2		14	55.0N	27	57.3W	FIDO	1139	Malfunction
	3		14	55.2N	27	57.5W	FIDO	1216	
<hr/>									
10552	1	12.VI	19	21.7N	29	54.1W	CTD	2110	2m 4683m
	2	13.VI	19	23.1N	29	53.6W	KASTEN	0038	
	3		19	25.8N	29	52.3W	FIDO	0326	
	4		19	21.1N	29	53.3W	ZODIAC	1007	
	5		19	21.1N	29	52.4W	BOX	1325	Pretrip 4175m
	6	13.VI	19	21.7N	29	51.4W	CTD	1631	
	7		19	24.5N	29	52.7W	P.W.S.	2237	Traversing gear seized 3½ hours 4735m 96%
	8	14.VI	19	25.4N	29	52.4W	FIDO	0144	
	9		19	27.3N	29	53.6W	BOX	0625	41cm 4655m
	10		19	21.3N	29	51.9W	CTD	1021	
	11		19	21.2N	29	52.±W	P.W.S.	1232	4745m 99%
	12						BOX	1607	Pretrip 4280m
<hr/>									
10553	1	16.VI	24	47.6N	27	31.6W	CTD	0500	

10554	1	18.VI	31	30.1N	24	29.2W	CTD	0307	2m 5370m
	2		31	29.7N	24	28.8W	KASTEN	0700	
	3		31	29.3N	24	28.0W	ZODIAC	0910	
	4		31	29.5N	24	28.3W	FIDO	1252	
	5		31	29.9N	24	26.1W	BOX	2038	59cm 5370m
	6		31	29.0N	24	25.2W	CTD	2239	
	7	19.VI	31	28.7N	24	24.3W	P.W.S.	0130	5371m 92%
	8		31	27.7N	24	25.5W	FIDO	0511	
	9		31	26.8N	24	23.8W	P.W.S.	1230	Mechanical malfunction
	10		31	29.3N	24	26.7W	BOX	1800	62cm 5370m
	11		31	27.3N	24	25.8W	KASTEN	2248	(Winch malfunction 30 min. (4m 5370m)
	12	20.VI	31	26.6N	24	26.8W	P.W.S.	0247	5371m 80%

NOTES TO TABLE 1

1. Times listed correspond to positions given; these are the closest available positions to the time of sampling.
2. Depths are uncorrected.
3. Abbreviations

BOX	IOS box corer. 30cm x 30cm area; depth of penetration as listed.
CTD	Brown conductivity, temperature and depth probe. Usually fitted with 10 General Oceanics GO-FLO bottles on rosette sampler.
FIDO	Filtration in the deep ocean. I.O.S. <u>in situ</u> large volume pumped filtration system.
KASTEN	Hydrowerkstätten Kastenlot square box gravity corer type 366: barrel length as listed.
NISKIN	Sampling bottles, 30L or 60L, worked from 4mm hydrowire.
P.W.S.	I.O.S. <u>in situ</u> pore water sampler. Mk II version, 8 ports, max sample volume 120ml total.
ZODIAC	Inflatable boat used for manual surface sampling away from ship.

