Shipboard Report

PALAEOFLUX

Sediment Traps Recovery

with

R.V. Ravello

4-10-1995 till 11-10-1995

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Shipboard Report of PALAEOFLUX

Mast-2 Programme MAS2-CT93-0051 (*)

For Sediment Traps Recovery

with R.V. Ravello (RV95)

from Baia (N. Naples) to Baia (N. Naples),

4-10-1995 till 11-10-1995.

Most of this report has been written on-board R.V. Ravello by G.de Lange and C. Corselli during the last Cruise of the PALAEOFLUX Programme. The report is distributed to the PALAEOFLUX coordinator (the responsable for EC communication), Directorate General XII Science Research and Development Marine Science and Technology MAST II, all the PALAEOFLUX partners (on request), and to the captain of the R.V. Ravello. Unauthorized use of the data contained in this report is considered unfair. Property of the data is of the PALAEOFLUX partners. Data exchange among partners is defined in Art. 7 of the contract MAS-CT93-0051 and Annex II, section B.

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CRUISE PARTICIPANTS

Although samples have been collected for a large majority of the PALAEOFLUX partners, the collection itself has been done by the Milano and Utrecht groups alone (Table 1). Technical support has been given by the Dutch Technical support Facility NIOZ-F.

Table 1. Cruise participants

person	task	Institute
C. Corselli	co-chief scientist	UM
G.J. De Lange	co-chief scientist	UU
H. De Waard	analytical technician	UU
A. Rutten	geochemical scientist	UU
J. Schilling	mechanical technician	NIOZ-F
L. Boom	mechanical technician	NIOZ-F

UM: University of Milano, Department of Earth Sciences Italy; UU: Utrecht University, Department of Earth Sciences,The Netherlands; NIOZ-F: Dutch Technical Support Facility at Netherlands Institute of Sea Research

INTRODUCTION

In the September/October 1994 expedition with R/V Urania the sediment traps were remoored at Urania Basin, one in oxic and one in anoxic conditions so as to compare fluxes and their preservation under different redox conditions (Objective 1 of the PALAEOFLUX Project). The traps must be released from the heavy bottom weight so as to be recovered. For safety reasons a double-release system is used, as the acoustic release signal does not penetrate across the seawater/brine density interface. The first (time) release was set to release the sediment-trap array so that it would rise to a few hundred meters above the brine interface, but still being attached to a rope. This time release has been set on October 1 at 00.00 hrs. From that time on there is an increasing risk to loose the equipment, 1-4 weeks still being an acceptable risk. The intention was to come and recover the sediment traps with the R.V. Urania during the first half of October 1995. At that moment, and being with a ship right above the site, the second acoustic release is released, and within an hour the array arrives at the surface. Unfortunately, R.V. Urania in 1995 and in particular during the critical time-frame (October 1995) was only available for a large National (Italy) programme, PRISMA, in the Adriatic sea. G. de Lange, C. Corselli and M.B. Cita have been trying to find an other ship for 'a free ride'. Amongst others 3 Russian ships, French and Italian vessels, military vessels returning from the Adriatic region and a Greek research vessel were attempted. Many collegues have been mobilized, but without success. In the end two alternatives have remained: 1. chartering the R/V ITALICA (approx. 80 kECU) to recover and remoor the sediment traps (essential for future researches and cooperations in the Mediterranean area), and 2. using the R/V RAVELLO (approx. 40 kECU) but only to recover the sediment traps. Despite the excellent judgement of the new project MESSAGE (MAST III), the project will not be funded to continue using the sediment traps in the Eastern Mediterranean. Consequently, the choice has been for the cheapest, and not for the scientifically most sound solution. Through the PALAEOFLUX coordinator G. Rothwell and finally directly by G. De Lange, it has been requested to obtain permission to use MAST-2 money for renting of the R/V RAVELLO. The answer from DGX11 MAST-2 has been rapid and positive, and although the samples from the sediment traps will be distributed to partners in France, Norway, United Kingdom, Italy and the Netherlands, the cost of shiptime (approx. 40 kECU) has been proposed to come from the Italian and Dutch allocated MAST-2 budgets alone.

CRUISE OBJECTIVES

The only Objective of this cruise was to recover the sediment traps that had been moored in Urania Basin. The two Technicap sediment traps (each with 24 bottles and a Tiltmeter) were used in the PALAEOFLUX Project for a quantitative study of elemental fluxes through water column and brines. This activity is one of the major efforts within Objective 1 of the PALAEOFLUX Project. The previous moorings have been extremely successful, giving results of seasonal biogeochemical fluxes, as well as large differences between oxic and anoxic samples. In addition, these samples are amongst the first to be recovered from the deep eastern Mediterranean. Although much speculation has been going on as for the possible productivity and amount of biogeochemical fluxes in the eastern Mediterranean, no continuous record of sediment trap sampling has thusfar been available. For understanding the functioning of the eastern Mediterranean eco-system it is absolutely necessary to know the biogeochemical fluxes leaving the surface waters and arriving at the bottom, and their subsequent preservation. This is not only of vital importance to the understanding of the present-day eastern Mediterranean and the modelling thereof, but also to that of the Paleo eastern Mediterranean system. It is therefore, that we decided to continue this mooring as long as possible. It is by relatively minor financial constraints that we have not been able to continue this mooring for an additional year (see under Introduction).

CRUISE NARRATIVE

The 1995 PALEOFLUX-5 cruise with R/V RAVELLO was in total very succesful. In only 4 days and 18 hours we covered more than 1100 nautical miles, carried out the retrieval of the sediments traps, and returned safely to the harbor of Baia (NA, Italy; Figure 1). The diary of the cruise is resumed on the Table 2 "Summary of operations".

Table 2. Cruise Narrative

3/10 arrival of the Dutch group in Naples
4/10 loading the equipment to ship; setting up laboratory
23 hrs departure
5/10 transit; setting up laboratory with the anoxic glove box
6/10 transit; continuing setting up laboratory
7/10: 05.00 hrs arrival at site at SE corner of the Urania Basin
05.30 - 06.15 hrs communication efforts with the sediment traps
06.15 release command given
06.55 hrs beacon and floats observed at surface;
7.30-11.00 hrs total string recovered and safely on-board
11.00-13.00 hrs samples removed from sediment traps, photographed, and securely stored in laboratory space under anoxic (lower trap samples), or under oxic (upper trap samples) conditions;
13 hrs start of transit and of processing of the samples;
8/10 continuing transit and processing of samples
9/10 continuing transit and processing of samples
9/10 arrival in Baia at 17.00 hrs
processing of samples continued
10/10 continuing processing of samples
11/10 continuing processing of samples

DETAILS OF THE VESSEL R.V. RAVELLO

Built in Norway, converted to a diving support vessel in 1978 by Bolnes Shipyard (Holland) and upgraded in Naples for scientific research and R.O.V. support. The ship is equipped with a newly installed (1993) Simrad ADP 700 Albatross Dynamic Positioning System for automatic station keeping and manual control.

PRINCIPAL DIMENSIONS overall length -82.32 m, breadth -13.30 m, draft -5/6.00 m, G.R.T. -1,581

PRIMARY PROPULSION SYSTEM N.2 WARTSILA diesel engines at 794 KW 1080 B.H.P. N.2 WARTSILA diesel engines at 586 KW 810 B.H.P. N.1 LIAANEN variable pich main propeller N.1 KAMEWA 600 B.H.P. Bow Thruster N.1 KAMEWA 600 B.H.P. Stern Thruster Cruising speed -10/11 knots Maximum speed -13 knots
Operating range -8,000 nautical miles

SATURATION DIVING SYSTEM n. 2 decompression chamber for a total of 10 divers n. 1 DRASS NF 062 diving bell (SDC) for 3 divers

SCIENTIFIC SUPPORT FACILITIES -300 square meters of free deck space for containers (10/20) -n.1 large air conditioned postprocessing laboratory -n.1 phothographic darkroom -n.1 Hydralift crane up to 30 tons. n.4 winches with 25 ton
maximum load n.2 four ton stern anchors n.2 nine ton bow anchors -Central Moon-Pool n.2 Atlas AFG fresh-water distillation units (daily capacity of 20 tons)

ELECTRICAL POWER PLANT n. 2 720 KVA diesel electric generators n. 1 857 KVA generator For a total of 1,700 KW with a power supply voltage of 380/220 three fase 50 hz

ACCOMODATIONS The vessel is equipped to accomodate 50 persons in single and double air-conditioned cabins, and with a recreation lounge.

Figure 1. R.V. Ravello at Baia (NA).

DETAILED RESULTS AND ACTIVITIES

Under favourable weather conditions (3 Beaufort NNE) we arrived on October 7 at 05 hrs at the site above Urania east-Basin (Figure 2), where two PPS-5 Technicap sediment traps had been moored nearly one year ago using RV Urania (PALAEOFLUX-3 cruise). The total mooring consisted of two sediment traps, two c

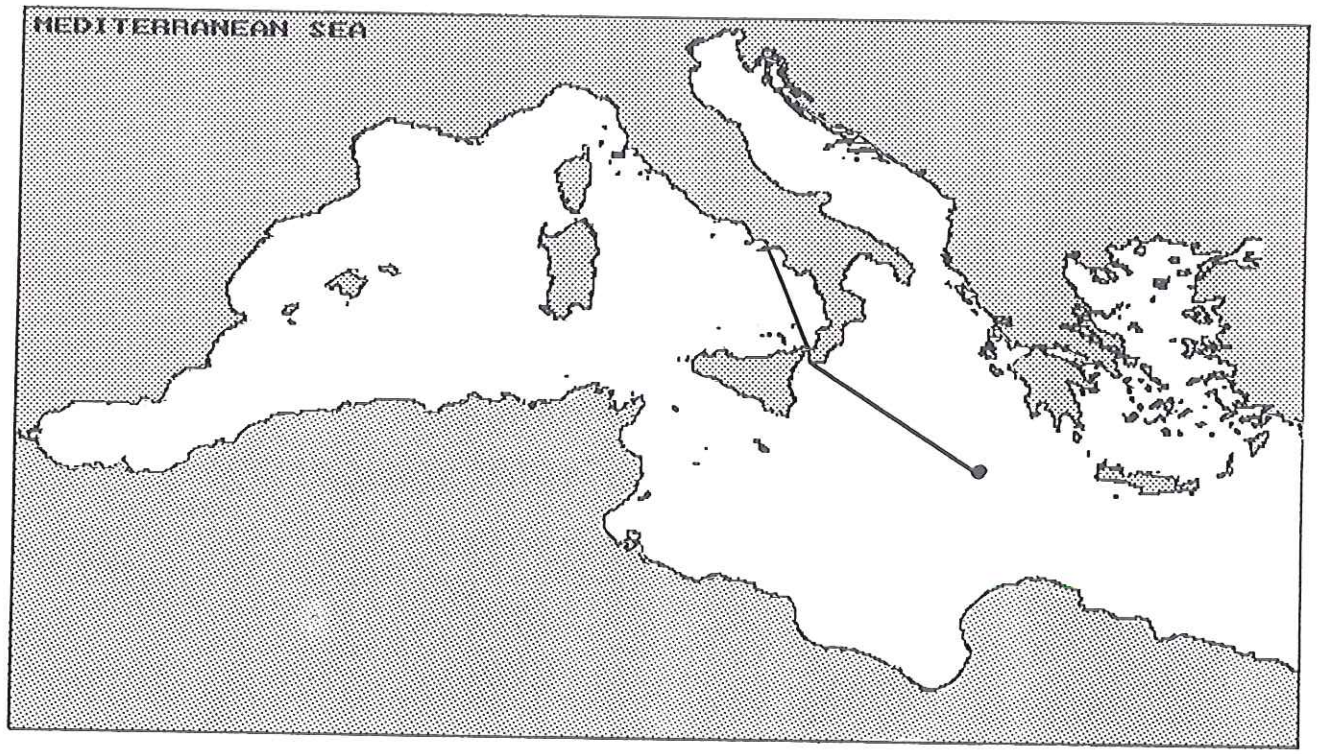

Figure 2. Map showing ship's track and sampling location, from Baia (NA) to Urania Basin, and back to Baia (NA) from October 7-11, 1995.

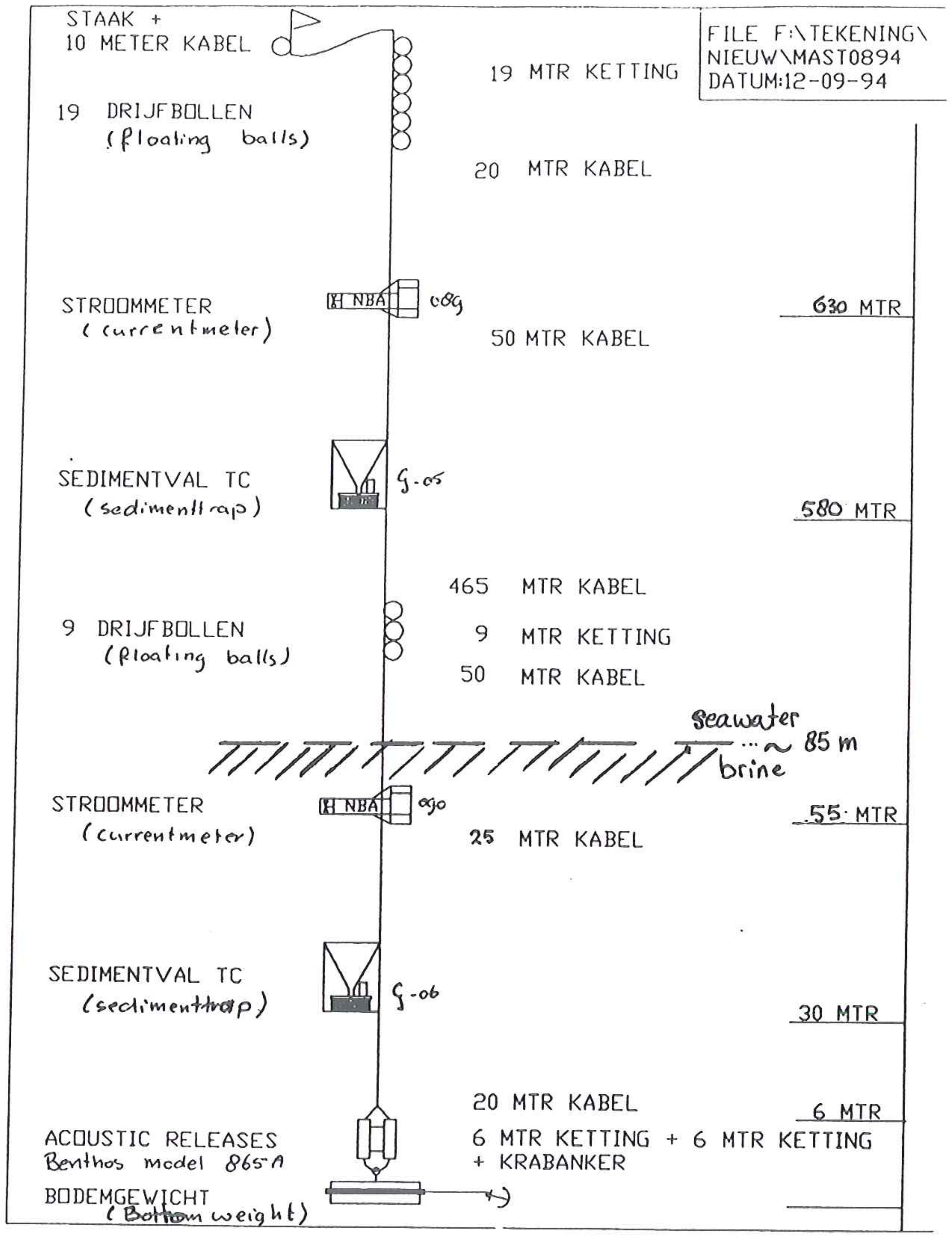

Figure 3. Schematic representation of sediment traps mooring that has been sampling in Urania east Basin from October 1994 to October 1995 (see text).

currentmeters (NBA nrs 89 and 90, upper and lower position respectively), two acoustic releases (Benthos 865A, but one with an optional time-release), a bottom-weight (approximately 900 kg) including a bloc with approximately 600 m of rope, 28 floating balls (Benthos), and a beacon with radar reflector (see Figure 3). In addition, a tiltmeter including pressure (depth), salinity, and temperature measurements had been mounted on each sediment trap.
As the initial position of the two acoustic releases is below the seawater/brine density interface (1.03 / 1.2 gr.cm^{-3}, it is extremely difficult for an acoustic signal to reach the bottom below this interface, i.e. to give the 'release' command. Therefore, a special construction was developed, that was subsequently used successfully several times at Bannock Basin, and which had been placed a year ago in Urania Basin. Briefly, one of the two releases was time-released, i.e. released at a pre-set time. In this case the time had been set on October 1 at 00.00 hrs. Subsequently, the rope and the whole mooring above the bottomweight, i.e. including the two acoustic releases would move upward approximately 600 m. This would bring the second acoustic release, that had not yet been released, well above the seawater / brine density interface. Consequently, this release should be released relatively easily. Before doing so, we usually make acoustic contact with both traps, so as to assess their depth. In all cases thusfar (see previous MAST-shipboard reports), the time release had functioned, and the rope had been fully unrolled. However, this time, no contact appeared possible with either acoustic release ! This could mean that both acoustic releases including the whole mooring had 'disappeared', or that both acoustic releases were malfunctioning, or that the time releases did not function properly, and that both releases were still below the seawater/brine density interface. Although no acoustic communication was possible between the ship (Benthos Release Communication Instrument) and the acoustic releases, this does not exclude that a much stronger acoustic signal such as when giving the '*release*' command would be able to reach the acoustic releases. Fortunately, this appeared to be the case, 40 minutes after giving the first release command, the mooring beacon was observed at the sea surface, exactly at the location below which the traps had been moored one year earlier. It soon became clear, that the time release had not functioned and still did not function at all for as yet unknown reasons. There were a few more remarkable things observed at the presently recovered mooring that were not found at previous moorings: there was considerable corrosion at all iron and zinc parts : bolts, split-pens, etc.. all were covered with a thick layer of black material, presumably pyrite (on the iron parts) and sphalerite (on the zinc parts). In addition, the lower chain at the acoustic releases was severely corroded, covered with black crusts, and being several mm thinner than the upper chain at the acoustic releases. The latter was slightly greyish, rapidly changing into a creamish colour (see picture, Figure 4), comparable to the 'normal' recovery of chains from previous Bannock Basin moorings. Furthermore, a thick crust (mud ?) was present on, and had 'streamlines' parallel to, the cilindrical housing of the acoustic releases. As the crust was at some places at least 1 cm thick, it seems unlikely that it was initiated by corrosion alone. At this moment, the more likely explanation is, that the mooring had sunk into the bottom mud until the upper part of the acoustic releases. This would explain not only the thick crust (mud) on the sides of the acoustic releases but would also explain the dramatic difference in

corrosion between the upper and lower chain at the acoustic releases. It must be noted that these chains are only approximately 1 m apart, but with extremely different corrosion characteristics (see above, and see Figure 4). If both chains would have been entirely in the brine, then there would have been no reason for a difference in corrosion, unless the bottom few decimeters of brine would have chemical characteristics that are extremely different from those in the brine immediately above it. The reason why the bottom sediments or possibly this bottom brine layer are so extremely corrosive remains to be explained. Unfortunately, no bottom sediments could be sampled during this 'emergency' cruise. During previous cruises bottom sediments have been sampled but no attempt was made to extract the porewater, or to measure pH and/or Eh in these sediments. It is highly recommended that such measurements will be done when they are sampled in any future cruise(s).

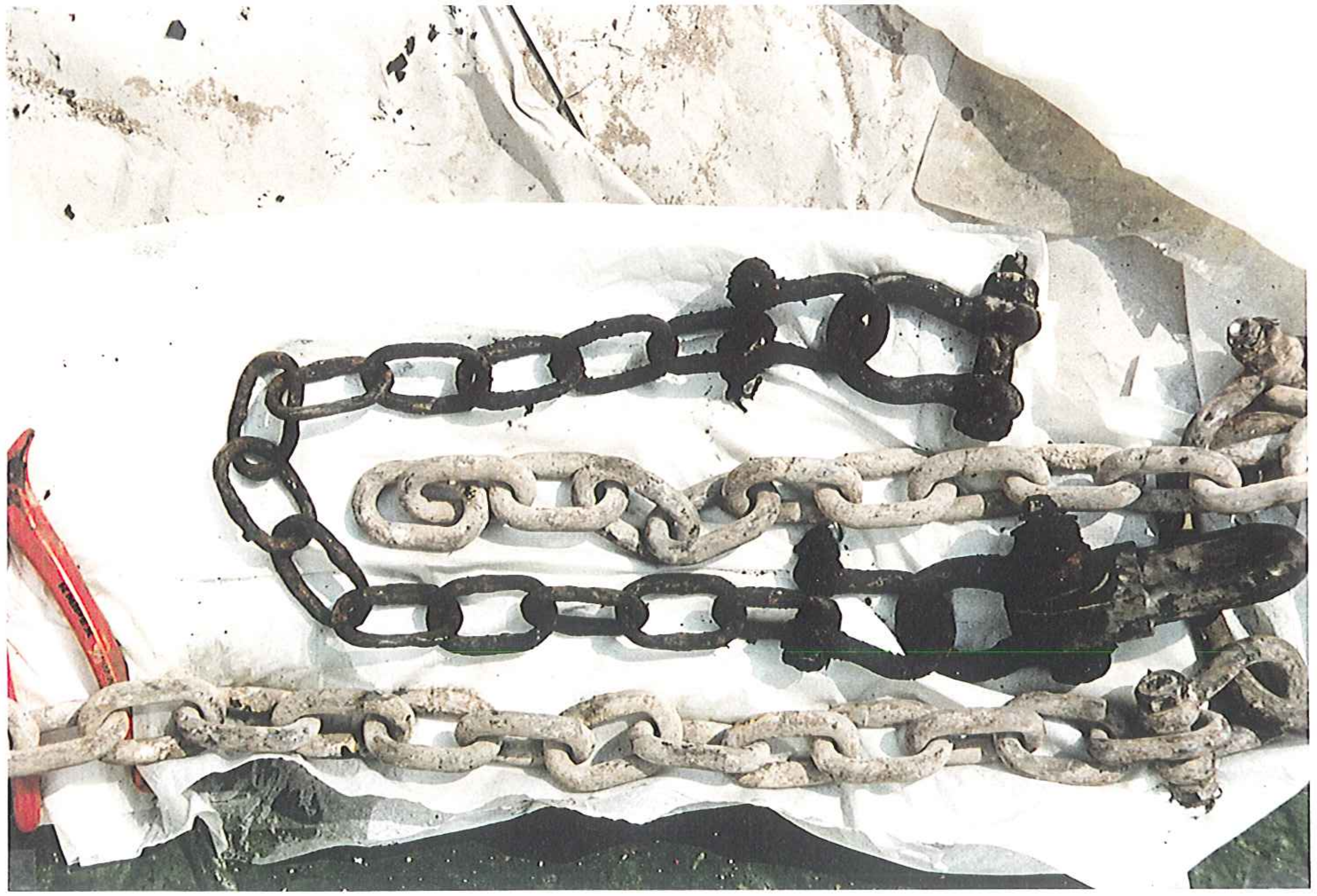

Figure 4. Picture showing the extreme corrosion that occurred with various parts of the 1994/1995 mooring in Urania basin; upper (light) and lower (dark) chains of acoustic releases..

In comparison to Tyro and Bannock Basins, it seems that only acidity combined with brine solutions could provoke such an extreme corrosion. However, any acidity should be removed rapidly, if 'normal'/ average Mediterranean sediments are present in Urania Basin. Such sediments contain 15-50% carbonate, hence would buffer the acidity immediately. Á possible way to create local acidic conditions could be: 1. by the oxidation of sulphidic water, 2. by emanating fluid reacting with the brine, and 3. by emanating hydrothermal fluids that usually have low pH i.e. high acidity. The first option is not very likely as the mooring was placed in the lower part of the Urania east Basin, which contains an extremely sulphide-rich brine (more than 10 mM sulphide), therefore, any oxidation of sulphide within this brine is highly unlikely. The last option, namely emanating hydrothermal fluids, is not impossible, but would at this stage be a pure speculation. One of the possible explanations according to option 2 is the reaction of upward migrating methane with high (brine) sulphate concentrations. From observations and analyses done during

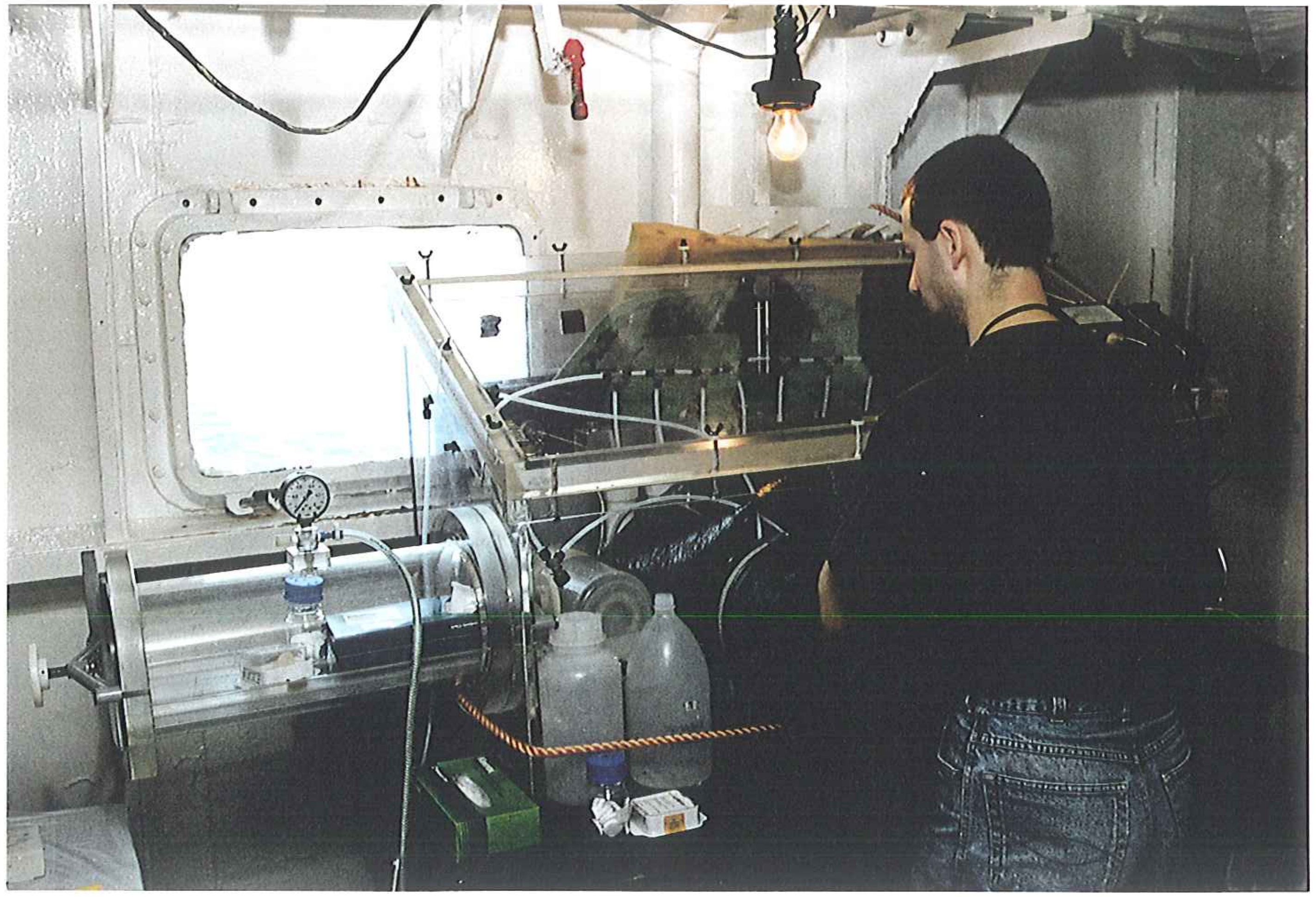

Figure 5. Glovebox in which anoxic sediment trap samples have been split and further processed.

and after previous cruises, it is known that the methane concentration as well as the sulphide concentration in Urania Brine is extremely high (see shipboard report Urania 1993 and 1994 (cruises MARFLUX-5 and PALAEOFLUX-3). The local emanation of methane could, already within the sediments, lead to a concomittantly emanating fluid that has become acidic according to the following equation :

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

At this very site the fluid will be acidic, but will rapidly loose most of its acidity due to a reaction with sedimentary (biogenic) carbonates, and with the bicarbonate-buffered brine. Although extremely high methane and sulphide concentrations were found in Urania Brine, there has been no evidence thusfar for methane-generated advective activity in the Urania east Basin. In addition, the structured temperature profile of the Urania east brine indicates that prior to and during the time of sampling in 1993 and 1994 (Urania shipboard reports), no such advective transport is likely to have taken place.

Sediment traps

The two traps were set to sample during identical time periods (see Table 3); the upper trap being located above- and the lower below- the seawater/brine interface (see Figure 3).
Samples from the two traps have been processed immediately on-board; those from the trap below the oxic seawater/ anoxic brine interface in a nitrogen-filled (anoxic) glovebox, those from above the interface at ambient atmosphere. However, exceptionally, samples 15 and 21 from the upper trap have been processed inside the anoxic glovebox too (see discussion below; Figure 5).
In general, each trap sample is split in 8 parts each equal to 1/8 of the total volume of the sample. Exceptionally, most of the samples from the lower trap have first been split into 8 equal portions; consecutively, 1 portion has been split again in 8 equal sub-portions. Such additional splitting has been done, as the amount of material recovered per sample has been approximately 50 to 1000-fold of that recovered in previous years while being moored in Bannock Basin (Figure 6,7).
The anoxic lower-trap samples all have darkgrey colours, with a distinct sulphide smell, whereas most of the oxic upper-trap samples were brownish except samples 13,14,15, and 21.

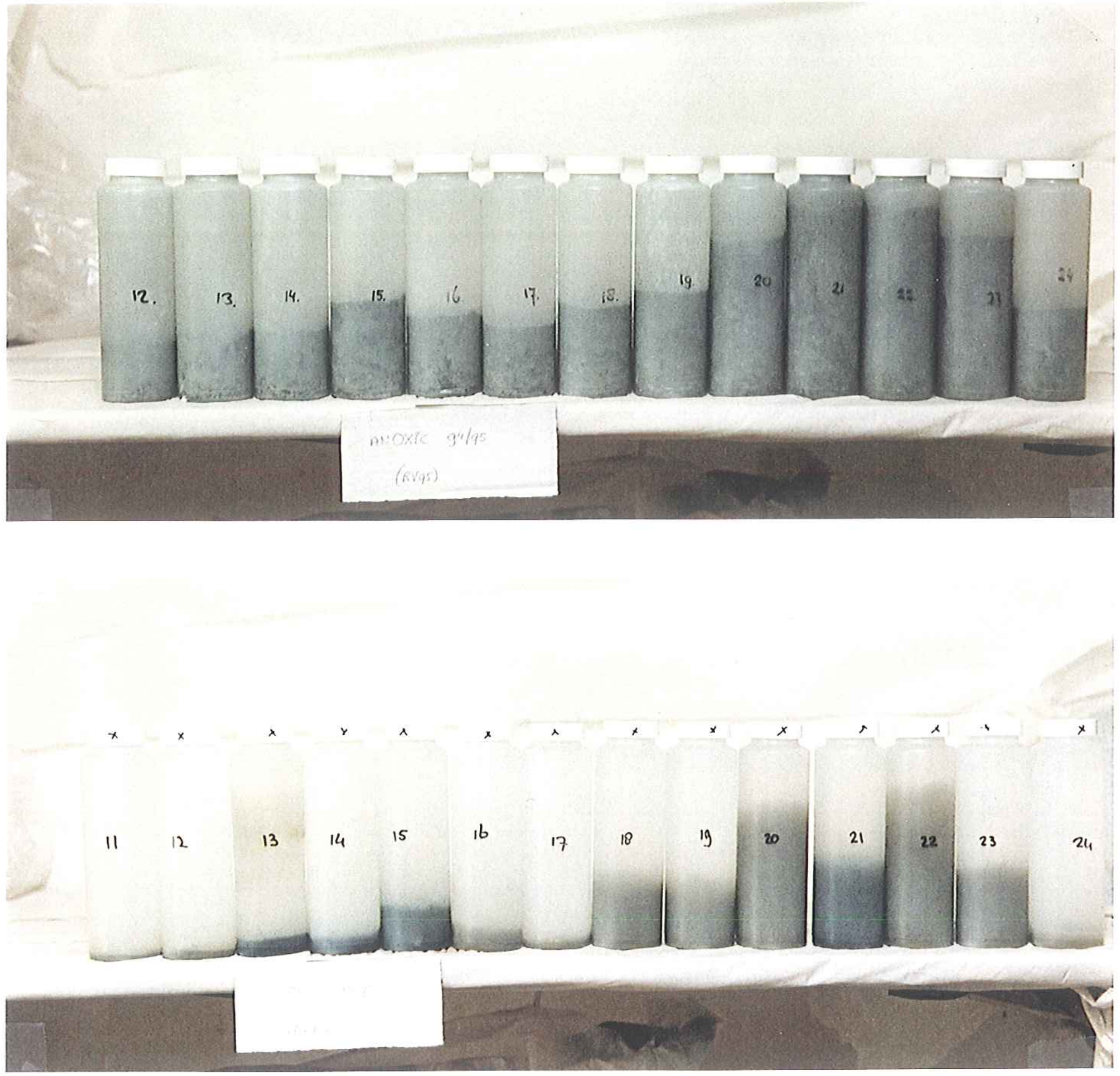

Figure 6. Picture of sediment trap samples taken immediately after recovery; upper panel darkgrey anoxic, lower panel brownish to darkgrey oxic samples. The darkgrey colour of the anoxic lower sedimenttrap samples is largely obscured due to gas bubbles sticking to the inside of the vessels

Table 3. Programmed sampling interval for the 1994/1995 PALAEOFLUX sediment trap deployment in Urania Basin east. Both traps have been programmed identical.

Sample	Interval	date of change (all at 01.00 hrs)
1	14 days	11-10-94
2	15	25-10-94
3	15	09-11-94
4	15	24-11-94
5	15	09-12-94
6	15	24-12-94
7	15	08-01-95
8	15	23-01-95
9	14	07-02-95
10	14	21-02-95
11	14	07-03-95
12	14	21-03-95
13	14	04-04-95
14	14	18-04-95
15	14	02-05-95
16	15	16-05-95
17	15	31-05-95
18	15	15-06-95
19	15	30-06-95
20	14	15-07-95
21	14	29-07-95
22	14	12-08-95
23	14	26-08-95
24	14	09-09-95
25	XX	23-09-95

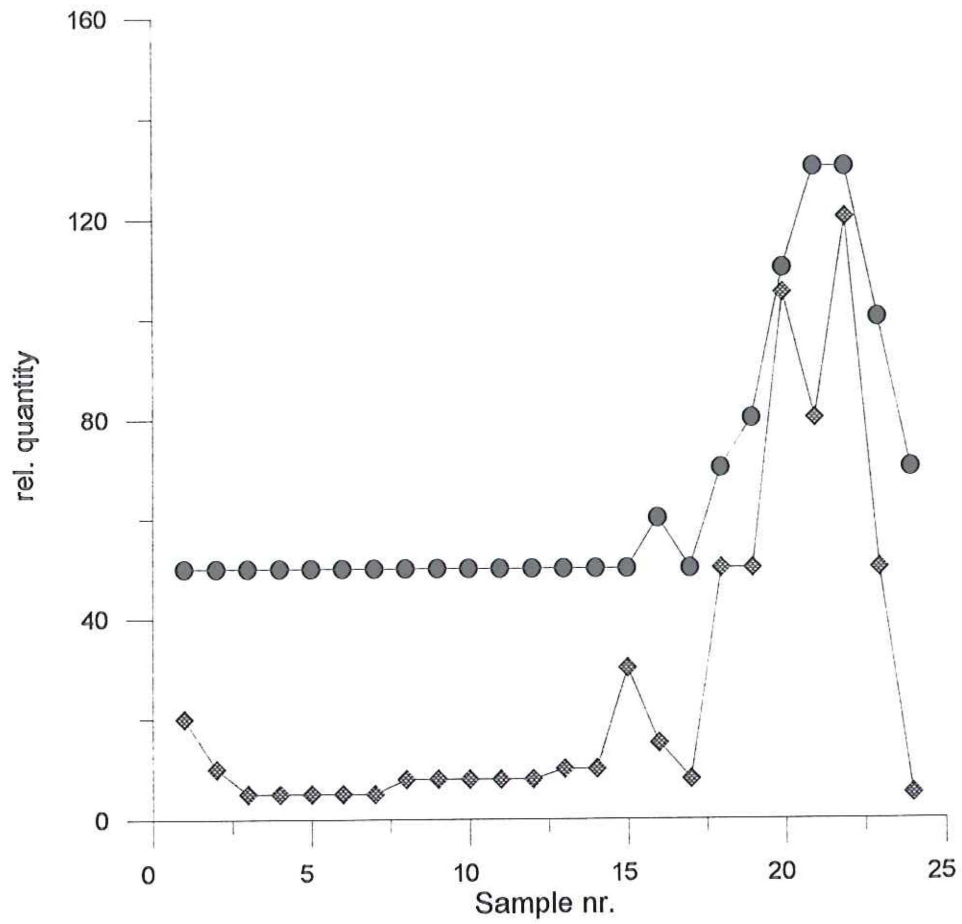

Figure 7. Relative quantities of recovered samples during the 1994/1995 sediment trap mooring in Urania Basin. The average of anoxic and oxic Bannock Basin samples recovered during previous years, was approximately 1 and 0.1 respectively on this scale.

It must be noted here, that one of the consequences of the refusal of the time-release has been that the anoxic sediment trap samples have been in an oxic water environment during only a few hours. It appeared that the sample vials are perfectly closed during even extended periods of time. Obviously, the salt-like crystals that were now found at the bottom of the sediment trap funnel, and between the coating and housing of the currentmeters would probably have disappeared upon extended exposure to normal seawater conditions. In addition, it must be noted that samples 15 and 21 from the upper sediment trap did contain black

particulate matter as well as overlying water with a distinct sulphide smell. In the case of sample 15 this means that either sulphide-enriched water was recovered in early May 1995, or that sulphide-enriched particulate matter was recovered generating sulphide to the overlying water in the vial. In both cases it demonstrates the vials to be extremely well closed for a period of 5 months.
A few remarkable features are visible in the preliminary estimates of the relative quantities of particulate matter recovered with the sediment traps:

1. The anoxic samples always recover much more material than the oxic samples of the same time interval. Referring to a similar situation in Bannock Basin such difference has been attributed to enhanced preservation and enhanced redeposition in the lower relative to the upper trap samples.

2. Upper- and lower- trap each received much more material at Urania basin than they did in Banock basin, during similar time intervals.

3. In two periods similarly enhanced recoveries are observed for upper and lower trap samples, most pronounced for the interval from June 15 - September 23 1995, i.e. an interval of approximately 3 months. These intervals of enhanced recoveries can be tentatively attributed to a naturel or to an anthropogenic process. The enhanced flux of particulate matter according to the latter hypothesis could be generated by nearby bottom-sampling activities (dredging, box- or piston-coring) during a period of ***at least*** 54 days. To the best of our knowledge there has been no scientific (i.e. bottom-sampling) activity around Urania basin during this time-frame nor a few months before and after it. Therefore, this explanation seems highly unlikely. The alternative explanation, i.e. that of naturel process(es) producing these intervals of enhanced recoveries of particulate matter is highly exciting and even more speculative at this moment.
One possible not entirely illusive pathway could be by a methane-generated eruption of anoxic mud reaching a level of at least 600 m above the seafloor !! The active eruption could have been in a number of pulses that have taken place in a period of at least 54 days, and that may still be continuing today ! Unfortunately, no CTD system was available on the R.V. Ravello. Consequently, no additional measurements could be made to confirm present or past activity. However, we are confident that if any such eruptive event occurred we should be able to detect this by current-meter, and/or tiltmeter annex salinity and temperature measurements. These data will be read and processed on-land, once all equipment is back in the laboratory.

Table 4. Preliminary observations sediment trap samples

	ANOXIC		OXIC	
nr.	mm	observ./colour	mm	observ./colour
1	50	d.grey	20	d.brown
2	50	d.grey	10	d.brown+rustbrown
3	50	d.grey	5	d.brown
4	50	d.grey+bubbles	5	d.brown
5	50	d.grey+bubbles	5	d.brown
6	50	d.grey	5	d.brown
7	50	d.grey+bubbles	5	d.brown
8	50	d.grey+bubbles	5	d.brown
9	50	d.grey+bubbles	8	d.brown
10	50	d.grey	8	
11	50	black+flakes	8	
12	50	d.grey+bl+bubls	8	
13	50	d.grey+bl	10	black + brown line (?)
14	50	d.grey	10	blakc
15	80	d.grey+bl	30	black+sulphide smell
16	60	d.grey+bl	15	brown
17	50	d.grey+bl	8	d.brown
18	70	d.grey+bl	50	greybrown
19	80	d.grey+bl+bubls	8	
20	110	d.grey	50	greybrown+flakes
21	130	dgrey+bl	50	black+sulphide smell
22	130	d.grey+bl	105	greybrown
23	100	d.grey	50	greybrown
24	70	d.grey	8	brown

(*): lightgrey flakes are present on top of the darkgrey/black samples 13,14 from the 'oxic' trap : indication of some oxidation? The oxic samples 13, 14 have been filtered under oxic conditions as there was no sulphide smell in the bottles, whereas the oxic samples 15 and 21 which had a distinct sulphide smell were handled/filtered under anoxic (nitrogen) conditions, similar to the anoxic samples.

It is remarkable that the black sulphide-smelling oxic sample 21 is followed by large quantities of brown (not black !) particulate matter in the oxic bottles 22 - 24. If the assumed 'eruptions' come from Urania Basin east, then one would expect all samples to be black, unless oxidation has occurred in the sampling vial. Alternatively, if the eruptions are relatively short pulses of a day or less, then, if such pulse is followed immediately by the closing of the bottle, the bottle contents may remain anoxic/sulphidic during a relatively long period, whereas if such event took place in the beginning of the sampling interval of that vial, then oxidation could take place during several days upto 14 days.
A similar effect would occur if the brown samples 22-24 were erupted nearby and were transported to this site, whereas the black samples 15, 21 must originate from the sediment almost immediately below the sediment traps. In this option several sources are needed, which makes it less likely.

CONCLUSIONS

Preliminary conclusions: The samples recovered from sediment traps moored at Urania basin east seem to be influenced mainly by brine related processes. The dramatic fluctuations in the estimated recovered amount of material may point to methane-generated mud eruptions reaching a level of at least 600 m above the local seafloor. Although all preliminary observations seem to point in this direction, this spectacular but still relatively speculative explanation needs to be confirmed by other, instrumental, observations, and future targeted sampling.

ACKNOWLEDGEMENTS

DIAMAR, and Captain Di Costanzo and crew of the R.V. Ravello are acknowledged for their fine cooperation. GOA/NIOZ-F are acknowledged for their flexible approach in the turbulently changing period and decision to (re)moor the traps in the eastern Mediterranean. We thank the EC MAST DGXII / Mrs. S. Johansson for their kind and rapid decision and communication to permit us to use MAST-2 funds allocated to the Milano and Utrecht groups to rent a vessel so as to be able to recover the sediment traps otherwise lost. We also acknowledge our respective families and friends for allowing us to go at sea (again) at such short notice. Professor M.B. Cita, dr. A. Tselepides, and many other collegues are thanked for their efforts in trying to obtain a vessel. CC and GDL thank Diego for his brief introduction into Paleo-Roman times.