



SCUOLA ESTIVA DI GEOMORFOLOGIA, ECOLOGIA E BIOLOGIA IN AMBIENTE MARINO E INSULARE TERZA EDIZIONE

PONZA 20-23.09.2022

Sala Comunale

SCUOLA ESTIVA DI GEOMORFOLOGIA, ECOLOGIA E BIOLOGIA IN AMBIENTE MARINO E INSULARE - TERZA EDIZIONE Ponza 20-23.09.2022

Federico Spagnoli

IRBIM-CNR, Università di Camerino -Scuola di Scienze e Tecnologie - Divisione di Geologia

La misura dei flussi all'interfaccia acqua-sedimento con camere bentiche e non

Istituta Seperiore per la Pratecione

e la Ricerta âmbientale

Misura dei flussi all'interfaccia acqua-sedimento con camere bentiche

Federico Spagnoli



CNR-IBIM Ancona, Università di Camerino -Suola di Scienze e Tecnologie - Divisione di Geologia



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What the dissolved benthic fluxes are?

- Fluxes of dissolved chemicals at the sediment-water interface
- Fluxes can be positive of negative that is released or adsorbed by the seabed sediments
- They are generated by
 - early diagenesis processes
 - fluids from high sub-bottom depths
 - by volcanic or hydrothermal processes



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Early diagenesis engine

- The biogeochemical reactions and processes occurring in the upper cm of the sediment
 - due to fall and accumulation of organic (OM) and inorganic (IM) matter on seafloor
 - Following organic matter deposition and degradation;
 - Mineral dissolution
 - Mineral precipitation



OM consits of:

Marine POC (mPOC), terrestrial POC (tPOC), aggregates or flocs of DOC

IM consists of:

IC, SiOx, trace elements, pollutants, others

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Federico Spagnoli: La misura dei flussi all'interfaccia acquasedimento con camere bentiche e non





 $(CH_2O)106(NH_3)16(H_3PO_4) <=>53CH_4+53CO_2+16NH_3^++H_3PO_4$

Methanogenesis

Sulfate reduction

 $(CH_2O)106(NH_3)16(H_3PO_4)+55SO_4^{2-}<=>106CO_2+16NH_3^{-}+55S^{2-}+H_3PO_4^{3-}+106H_2O_4^{-})$

 $(CH_2O)106(NH_3)16(H_3PO_4)+212Fe_2O_3+848H+<=>424Fe^{2+}106CO_2+8NH_3^-+H_3PO_4^{3-}+530H_2O_4^{3-}+50H_2O_$

Oxi-hydroxi-Fe reduction

 $\begin{array}{l} Oxi-hydroxi-Mn-reduction \\ 5(CH_2O)106(NH_3)16(H_3PO_4)+236MnO_2+472H+<=>236Mn^{2+}106CO_2+8N_2+H_3PO_4^{3-}+336H_2O_4^{3-}+36H_2O_4^{3-}+3$

Denitrification (Nitrate reduction) $5(CH_2O)106(NH_3)16(H_3PO_4)+472HNO_3 <=>236N_2+520CO_2+5H_3PO_4+886H_2O$

Anaerobic biodegradation

 $(CH_2O)106(NH_3)16(H_3PO_4)+138O_2 <=>106CO_2+16HNO_3+H3PO_4+122H_2O_4$

Aerobic biodegradation

Red: Organic matter degradation products

Early diagenesis processes

Blue: final electron acceptors

Schematic way of organic matter breakdown in anaerobic sediments



Particulate organic matter (POM) is initially hydrolyzed to High Molecular Weight Dissolved Organic Matter (HMW-DOM), which is then further hydrolyzed and fermented to monomeric Low Molecular Weight Dissolved Organic Matter (mLMWDOM).

The terminal oxidation of **mLMW-DOM** is coupled to the reduction of terminal electron acceptors [largely sulfate (**SO4**₂) in marine systems, but also iron and manganese oxyhydroxides (such as Mn(OH)₂, Fe(OH)₃) and nitrate (**NO**₃), producing dissolved inorganic carbon (**DIC**), methane (**CH**₄), ammonium (**NH**₄⁺) and phosphate (**PO**₄**3**⁻) as terminal end products of organic matter mineralization, as well as hydrogen sulfide (**H**₂**S**), reduced iron (**Fe**²⁺) and Mn (**Mn**²⁺) and dinitrogen gas (**N**₂) as the reduced forms of the electron acceptors.

Some fraction of **HMW-DOM** is degraded into **p**olymeric **L**ow **M**olecular largely refractory and unavailable to the sedime**W**eight **D**issolved **O**rganic **M**atter (**pLMW-DOM**) which is nt microbial community.



Early diagenesis processes generate dissolved fluxes at the sediment-water interface

- Outward the sediment
- Inward the sediment

Factors affecting Early Diagenesis Processes

- High fresh organic matter contentsHigh productivity
- Presence of Fe an Mn Oxi-Hydroxides
- High sedimentation rates
- Fine grain-size
- •Limited resuspension processes



Dissolved fluxes at seafloor in volcanic environment Panarea Volcanic Comples (PVC)



Fluids and gases ascent and seep in volcanic environment





Graph of the DIC fluxes measured at seafloor interface around the PVC.

Location and graphical view of the DIC fluxes in the Smoking Land Valley and the *Secca dei Pesci*.

(Spagnoli et al., submitted)



The dissolved fluxes at the sediment-water interface can be measured or calculated by different methods www.wikiwand.com/en/Eddy covariance

- Measured
 - In situ

• In lab

- Benthic chamber deployments
- Eddy covariance



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Calculated

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10:30:17



Eddy covariance



What a benthic chamber is

Basic principles to study early diagenesis processes by benthic chamber deployment

The benthic chamber measures the fluxes of dissolved substances at the sediment-water interface

- A benthic chamber is a box placed over the bottom sea with a sealed top and an open bottom;
- Types of benthic chambers range from very simple to very complex for shallow and deep environments.





The evolution of CNR benthic chambers



Hammond, Giordani, Frascari, 1984



Spagnoli & Frascari, 1984



Spagnoli & Masini, 1996



Doug Hammond, 1984, USC, USA

Spagnoli et al., 2010



sensors

The AMERIGO Lander and the Automatic Benthic Chamber (CBA): Two New Instruments to Measure Benthic Fluxes of Dissolved Chemical Species ⁺

Federico Spagnoli (*, Piechaigi Penna 1, Giordano Giuliani), Luca Masini ¹ and Valler Martinetti ¹ Juliun parle Biones Biologiche ele Bioreenlagie Madee (BBBM), Carsiglio Nationale delle Biordee (NDR), 8012 Autoritationale piechaige pennest ani 17 21, alexicas galazziorari (x.G.) ² Instituti el Nationalettationa Mistory vanto chaigio Nationale di Externite, 41202 Biograp, Italia

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Corraspondersee federice spagnehetenzit; Tele (39-071-20/884)

¹ The paper lease sciencid synchrone paper phylicide of Spegnell, 5: Clarine, G.; Kostinall, V.; Model, L.; Pouze, P. (MESOC and Clar. A new hadre and a new assessible build chamber or haveled both the new more science single and science single and science science and the science science

Received: 28 April 2019; Accepted: 5 June 2019; Published: 10 June 2019

Abstack Marke ordenments are concently wells for a range collegical generator have bool and optical antipopt services, each or public metals and antisoptical implies, should also use as our additionton and varanting. These strains can result in hisperchetal each variations, environmental policities, and concept in building each coupling processes. These set derives, the amongle cancel and the Automatic Denhite Chandre (CMA), have been developed in accesses the large of distribution, and concept in building each coupling processes. These strategies are able of distribution, and concept in building each coupling and the value column, to access the strain of the coupling of the coupling of the strate strategies and the strate column and amongle chair near approxima includes as well and approxime (gets 100 Ma) when out the opphyra arrange of information and the coupling to 300 m. The strate couple and the opphyra arrange of thermounds in a strate of the possible to building accoupling the strategies of the opphyra of a strategies of a variave of the couple's table and approximation and the conception of the data when the outer of the management than data show good agreement integra conception the strategies of the strategies of the possible of the strategies of the management that data show good agreement and each data more out while possible of the strategies o

Keywonds lander: benthic chambers; benthic fitnes of dissolved chemical species; morineicchnology; marine instrumentation

Spagnoli et al., 2014



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The present CNR benthic chamber an Lander

AdaN

Amerigo



Spagnoli et al., 2019

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AdaN (Ada Natali, Massa Fermana (FM), 5 marzo 1898 – 27 aprile 1990. First woman major after WWII)

The automatic benthic chamber AdaN is made by a polymethylmethacrylate cylinder (80 cm ID, 33 cm h) closed on the top and open on the bottom



AdaN is equipped with:

- A device for collecting water samples inside or outside the chamber or to inject a tracer inside the chamber (the VAMPIRE);
- A multiparametric probe (Hydrolab MS5) to measure oxygen, pH, Eh, temperature, conductivity (i.e. salinity) inside the chamber;
- Simple and commercial available electronic (Idec MicroSmart FC6A PLC);
- Batteries.







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AdaN deployment

AdaN can operate on the continental shelf (up to 200 m depth)



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la Ricerta âmbienta



AdaN, Multiparametric probe data



PANA14-BP, Depth, ORP

18:28

Time (hh:mm)

24

23

23

22

22

21

16:04

17:16

Depth (m)

- Salinity step
- Increasing temperature
- Decreasing pH
- Decreasing O2
- Changing depth

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19:40

200

100

-100 J -200 dg

-300

-400

-Depth

-ORP

20:52

(m<

0



Depth and ORP

Video CB Landing

Da tagliare

PONZA 20-23.09.2022 TUNLA LU-LJ.UJ.LULL

CASE3 SCUOLA <mark>estiva</mark> di **Geomorfologia, ecologia** e <mark>biologia</mark> in ambiente marino e insulare -H 29 D 17 06:27:11 02/02/11

The lander Amerigo

On board

Landing set up





A lander is a device that reach the sea bottom by controlled falling due to the gravity

Main components



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The Lander Amerigo



Main characteristics

- Amerigo is a lander (able to reach (by controlled gravity falling) and operate on the sea bottom and return (by controlled buoyancy) to the surface autonomously;

-At present is configured for the measurement of dissolved fluxes at the sediment-water interface, including dissolved gases, nutrients, metals and pollutants;

- it is prepared to host other instruments for different monitoring and measurement studies:

- sensors for water column (oxygen, pH, methane, PAHs, pCO₂, H₂S, turbidity, fluorimeter);
- Instruments: microprofiler, (sediment-water interface properties), penetrometer (mechanical properties of the surface sediments), gravimeter, wave and current meter, corer.

Amerigo can operate from continental shelf to abyssal plain (up to 6000 m depth).

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Amerigo Equipment: Devices for the dropping, landing and rising

Ballasts for Controlled gravity falling





Radio, flash and GPS for the recovery



The buoy array for the rising



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Amerigo

3 benthic chambers (for dissolved flux measurements at the sediment-water interface)



Benthic chambers

- polymethylmethacrylate cylinder, 37.5 cm ID, 15 cm h;
- Open lid;
- Rotating paddle;
- Collecting syringes;
- Sensors;
- Oxistat;
- Landing carousel.

Benthic chamber (top view)

Benthic chambers (lateral view)







Amerigo equipment: devices for collecting water samples and oxygen replacement

VAMPIRE. Device for collecting water samples inside and outside the chamber and to inject tracers



OXYSTAT. Device for replacing oxygen inside the chambers



Glass ampoules for collecting gas samples





The Vampire

Archivio-1_foto e filmati strumenti- 1_da_elaborare-A_case 4_filmati-case4videorov-DVD3-videotslanciatutti-video_ts.ifo-

da 8:41:16 a 8:43:20









Amerigo equipment: The electronic

The in house made electronic

- microprocessor Atmega128, 2 RS232 ports, 1 RS485 port; 3 analogic ports, 19 on/off ports, in a glass sphere;
- 12V rechargeable Pb batteries in two glass spheres.





The glass sphere housing of the electronic and batteries (up to 700 bars)



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The Amerigo Lander: Other devices (to monitor the activity)

The video camera

(Telesub Lanterna)



The CTD

(SBE 37-SI MicroCAT)



AMERIGO at work



Survey activity





AMERIGO: technical data







AMERIGO: Sensor data

Oxygen in Benthic Chambers 1, 2 and 3





AMERIGO, Sensor data



Turbidity in Benthic Chamber 1 and 2

Methane in Benthic Chamber 1



Video Lander Amerigo



Amerigo and AdaN: Water sample treatment and analyses

other metals, etc.).

On board



Water sample separation and conservation treatments in inert atmosphere for the following chemical analyses

Laboratory analyses





On board analyses



Dissolved flux calculations

Dissolved fluxes at the sediment-water interface are calculated by:

- Dividing the concentration of each chemical species (measured in the water samples collected or measured by probes, inside the chamber) by the time of collection/measurement
- Multiplied by the volume of the chamber
- Divided by the bottom area of the chamber

 $J = \frac{\partial C_i}{\partial t} \ (V/A)$

J = Flux at sediment-water interface C_i = Concentration of i^{th} chemical compound t = time of measurement V = actual volume of the chamber A = bottom area of the chamber



J = m * h m = angular coefficient (slope) of the C_i/A - t<math>h = height of the benthic chamber



Determination of real internal volume of the chamber

The real volume of the chamber during the deployment is determined by injecting a tracer (CsCl or deionized water) in the chamber

 $V_2 = \frac{\partial V_1}{C_1} C_2$

- C_1 = Concentration of tracer laboratory solution V_1 = volume of the tracer injected
- C_2 = concentration of the tracer inside the chamber V2₂ = actual volume of the chamber







AMERIGO and AdaN data comparison

DIC surface concentration in Benthic Chamber 1, 2, 3 and AdaN (L.V.)

DIC benthic fluxes in chamber 1, 2, 3 and AdaN (L.V.) and previous data





Sediment-water flux calculation from pore water chemical composition

Calculated benthic fluxes

$$J_{i} = -\emptyset D_{i} \left(\frac{\partial C_{i}}{\partial z} \right)_{z=0} \qquad \begin{array}{l} \emptyset = \text{porosity} \\ D_{i} = diffusion \ coefficent \end{array}$$

The diffusive exchange of solutes through the Sediment-water interface can be calculated from concentration gradients along the sediment water boundary by applying Fick's first law of diffusion

(Berner, 1980)



concentration gradients at the Sediment-water interface



Early diagenesis studies

Early diagenetic processes are investigated by sediment cores collected by SW104 corer.







In-situ profiling with a microprofiler (MPI Bremen/AWI)

On-board profiling with a microprofiler (CNR)



Pore water microprofiling at the sediment-water interface







Calculated benthic fluxes

 $\mathbf{F}_{\text{total}} = \mathbf{F}_{\text{diff}} + \mathbf{F}_{\text{irr}} + \mathbf{F}_{\text{adv}}$

where

F_{total} is the total benthic fux
F_{diff} molecular diffusion
F_{irr} irrigation
F_{adv} advection

Calculated (diffusive) fluxes (mmol/m²*day)



Gradient at z=0



First approach: $\frac{C_{i(w)}}{C_{i(z_1)}}$ $C_{i(w)}$ = Concentration of *i*th chemical compoundin near sea bottom water $C_{i(z_1)}$ = Concentration of *i*th chemical compoundin in the first near surface core sediment sample



$F_{total} = F_{diff} + F_{irr +} F_{adv}$ where

F_{total} is the total benthic fux F_{diff} molecular diffusion F_{irr} irrigation F_{ady} advection

$$\frac{\delta C}{\delta t} = Ds \left(\frac{\delta^2 C}{\delta z^2}\right) - w(1+K) \left(\frac{\delta C}{\delta z}\right) + R_z + I_z = 0$$
 General diagenetic equation (Berner, 1980)

Ds = diffusion coefficient z = depth w = accumulation rate $R_z = adsorption-desorption$ $I_z = irrigation$



Calculated benthic fluxes





Measured and calculated bethic fluxes

Measured fluxes from the benthic chamber

Calculated fluxes from pore waters

$$J = \frac{\partial C_i}{\partial t} V / A$$

$$J_i = -\emptyset D_i \left(\frac{\partial C_i}{\partial z}\right)_{z=0}$$

- Irrigation
- Bad definition of sediment water interface gradient



Measured and calculated benthic fluxes



- Benthic fluxes generally decrease from Po River mouths (increasing distances from main sediment and nutrient sources, continuous reworking, lower primary production, less reactive organic matter)

- Negative DIC fluxes in central Adriatic and Ionian slopes (DIC sediment trap?)







Tests and simulations

LIMNOLOGY and OCEANOGRAPHY

Limmol. Oceanogr. 9999, 2019, 1–16 © 2019 Association for the Sciences of Limnology and Oceanography doi: 10.1002/Ino.11357

Seasonal variability of calcium carbonate precipitation and dissolution in shallow coral reef sediments

Laura Stoltenberg ^(D), ^{1*} Kai G. Schulz, ¹ Tyler Cyronak ^(D), ² Bradley D. Eyre ^(D)

¹Centre for Coastal Biogeochemistry, School of Environment, Science, and Engineering, Southern Cross University, Lismore, New South Wales, Australia

²Halmos College of Natural Science and Oceanography, Nova Southeastern University, Dania Beach, Florida

Abstract

Shallow, permeable calcium carbonate (CaCO₃) sediments make up a large proportion of the benthic cover on coral reefs and account for a large fraction of the standing stock of CaCO₃. There have been a number of laboratory, mesocosm, and in situ studies examining shallow sediment metabolism and dissolution, but none of these have considered seasonal variability. Advective benthic chambers were used to measure in situ net community calcification (NCC) rates of CaCO₃ sediments on Heron Island, Australia (Great Barrier Reef) over an annual cycle. Sediments were, on average, net precipitating during the day and net dissolving at night throughout the year. Night dissolution rates ($-NCC_{NIGHT}$) were highest in the austral autumn and lowest in the austral winter driven by changes in respiration (*R*) and to a lesser extent temperature and Ω_{arag} /pH. Similarly, precipitation during the day ($+NCC_{DAY}$) was highest in March and lowest in winter, driven primarily by benthic net primary production (NPP) and temperature. On average, sediments were net precipitating over a diel cycle (NCC_{24h}) but shifted to net dissolving in July and December. This shift was largely caused by the differential effects of seasonal cycles in organic metabolism and carbonate chemistry on NCC_{DAY} and NCC_{NIGHT} . The results from this study highlight the large variability in sediment CaCO₃ dynamics and the need to include repeated measurements over different months and seasons, particularly in shallow reef systems that can experience large swings in light, temperature, and carbonate chemistry.



Benthic chambers and landers



Side and front views of the chamber assembly.

Glass floats (1 of 8) Main ballast release Secondary ballast release 1 of 3) Electronics pressure case Sampling racks Syringes Expendable ballast Chamber lid and stirring mechanism Chamber & chamber scoop

Titanium chamber (9)

chamber lid (10),

gasket in the upper edge of the chamber against which the lid seals (11)

chamber water stirring mechanism (12)

scoop for recovering the sediments within the chamber at the end of the experiment (13)

hydraulic cylinder (1 of 2) which closes the scoop (14)



Jahnke and Christiansent, 1989

Other benthic chambers



Gotheborg benthic lander recovery

Benthic chamber with syringes samplers



Lee et al., 2015

The KIOST benthic lander

	Specification
Frame materials	SUS312
Chamber materials	PVC
Water sampler materials	SUS316
Height (cm)/Weight (kg)	250/550
Positive buoyance (kg)	~ 62
Chamber area (cm ²)	841
Stirring speed (rpm)	30-35
Acoustic release	Teledyne Benthos, 865-A
DC power (V)	17 V
DO sensor	Aanderra Oxygen Optode 4330DW



Recovery of the benthic lander (A)



Ultra-landers (11000 m depth)



Figure 1. (a) Locations of available in situ benthic O₂ flux data from hadal settings. The black dots represent the sites reported in Wenzhöfer et al. (2016). The are the lander deployment sites of this study. The yellow dot represents the overlapped site of this study and Glud et al. (2013). (b) Overview of the stuce locations of lander deployment sites reported in this study (red dots). (c) Picture of the lander (Lander-III) prior to deployment.

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Geophysical Research Letters

RESEARCH LETTER 10.1002/2017GL076232

Key Points: Total oxygen uptakes were measured for the first time in hadal tenches using in situ benthic chamber incubators augusts that nates of benthic carbon mineralization reflect the surface ocean productivity However, factors governing the diagenetic activity in hadal tenches apparently include supply of terrential organic material

> Supporting Information: Supporting Information S

Correspondence to

M. Luo and B. Pan.

mluo@shou.edu.cn; bbpan@shou.edu.cn

Luo, M., Glud, R. N., Pan, B., Wenzhöfer,

Benthic carbon mineralization in hadal

trenches: Insights from in situ determi-

F., Xu, Y., Lin, G., & Chen, D. (2018).

Citation

ER Benthic Carbon Mineralization in Hadal Trenches: Insights From In Situ Determination of Benthic Oxygen Consumption

Min Luo^{1,2,3} ⁽²⁾, Ronnie N. Glud^{4,5} ⁽²⁾, Binbin Pan¹ ⁽⁰⁾, Frank Wenzhöfer^{6,7} ⁽²⁾, Yunping Xu¹ ⁽²⁾, Gang Lin¹, and Duofu Chen^{1,2}

¹Shanghai Engineering Research Center of Hadal Science and Technology, College of Marine Sciences, Shanghai Ocean University, Shanghai China, ¹Abaoratory for Marine Science and Technology, Qingdao, China, ³College of Earth Science and Engineering, Shandong University for Science and Technology, Qingdao, China, ⁵Nordic Centre for Earth Evolution, University of Science more Demmark, ⁵Department of Ocean and Environmental Sciences. Toky Ohior Sciences 1, 2019. Construct Centre for Barth Evolution, University of Science and Technology, Olingdao, China, ⁵Nordic Centre for Earth Evolution, University of Science and Technology, College and Sciences. Toky Ohioress 1, 2019. Construct Center for Polar Marine MicroBiology, Bremen, Germany, ²Alfred-Wegener-Institute Helmholtz Center for Polar and Marine Research, Bremenhaven, Germany

Abstract Hadal trenches have been proposed as depocenters of organic material and hot spots for organic matter mineralization. In this study, we for the first time quantified the total benthic O₂ uptake in hadal trenches using in situ chamber incubations. Three trenches in the tropical Pacific were targeted and exhibited relatively high diagenetic activity given the great water depths, that is, the Mariana Trench (2.0×10^2 µmol O₂ m⁻² d⁻¹, 7.011 m), and the New Britain Trench ($6.0 \pm 0.1 \times 10^2$ µmol O₂ m⁻² d⁻¹, 7.011 m), and the New Britain Trench ($6.0 \pm 0.1 \times 10^2$ µmol O₂ m⁻² d⁻¹, 7.011 m), and the New Britain Trench ($5.0 \pm 0.1 \times 10^2$ µmol O₂ m⁻² d⁻¹, 7.011 m), and the first first of total organic carbon and a¹³C of total organic carbon in the sediments and previously published in situ O₂ microprofiles from hadal settings, we suggest that hadal benthic carbon mineralization partly is governed by the surface production and also is linked to the distance from Inad. Therefore, we highlight that terrestrial organic matter can be of importance in sustaining benthic communities in some hadal settings.



Figure 2. O₂ concentrations measured during chamber deployments at the trench axes of the (a) Mariana Trench, (b and c) the Mussau Trench, and the (d and e) New Bitain Trench. The arrows indicate the time when the lids were closed and incubations started. Straight lines represent the linear regression fits to the measured O₂ concentrations. Due to malfunctioning of the newly customized optodes, we only successfully obtained one set of O₂ data from the Mariana Trench and two sets of O₂ data from the Mussau Trench and the New Britain Trench, respectively. Data were provided by one oxygen optode in each chamber.



- (A) Autonomous Underwater Vehicle (AUV ABYSS);
- (B) Ocean Floor Observing System (OFOS);
- (C) Remotely-Operated Vehicle (ROV Kiel 6000);
- (D) teleoperated crawler of ONC (Ocean Networks Canada: http://www.oceannetworks.ca);
- (E) stationary lander system (these can also be equipped with baited traps, as shown in the image).





Brandt et al., 2016

Cutting the Umbilical: New Technological Perspectives in Benthic Deep-Sea Research

Autonomous seafloor vehicle:

combination of central lander and mobile robot for operations of up to 6 km the crawler returns to the central station to transfer the data and recharge it batteries (http://www.robex-allianz.de/en/). Source: Geomar; design: Meyer.







Hydrate Ridge

Regional Scale Nodes study sites (Hydrate Ridge)

The real-time interactive capabilities of the cabled observatory are critical to studying gas-hydrate systems because many of the key processes may occur over short time scales and will require adaptive response and sampling capabilities that include fluid sampling, increases in data accumulation rates and imagery from cameras, and in situ manipulation of chemical sensors (OOI Website).





Technology development

Pressured-core-sampling systems (Abegg et al., 2010; DAPC, Pape et al., 2010);

Example of Pressure Core Sampler



MeBo-Pressure Core Sampler (MDP, left and middle) for use with MeBo and MDP for use in free-fall mode (right). BMWi Project SUGAR II

New researches in the gas hydrate field, Rome, 19/09/2014, CNR-CAGE-MISE-RSE meeting

ARE - TERZA EDIZIONE





Special funnel to collect samples of natural gas bubbling up from the seafloor. Image: © 2003 MBARI



The absolute quantity of natural gas within the core, whether dissolved in pore fluid, frozen in hydrate, or even present as free gas, can be measured in the laboratory through controlled depressurisation experiments. (GEOTEK Ltd)



