11th International Conference on

Gas in Marine Sediments

4-7 September 2012

Nice, France

Congress Schedule

Information, and Abstracts

Host

The conference is hosted by the Centre National de la Recherche Scientifique (CNRS), France.

Local Organizing Committee

Catherine Pierre
Giovanni Aloisi
Ioanna Bouloubassi
Sébastien Duperron
Jeffrey Poort
Jean Mascle
Sébastien Migeon
Stéphanie Dupré
Germain Bayon
Karine Olu-Le Roy
Laurent Toffin

The GIMS11 conference will be held at “la Maison du Séminaire”

29 Boulevard Franck Pilatte, 06300 Nice (http:www.maisonduseminaire.eu)

Programme overview

	Morning	Afternoon	Evening
Tuesday **September 4**	09:00-10:00 Registration 10:00-10:30 Welcoming address 10:30-11:00 Coffee break **11:00-12:30 Talks** 12:30-14:00 Lunch	**14:00-15:45 Talks** 15:45-16:15 Coffee break **16:15-18:00 Talks**	19:00-20:00 Ice breaker
Wednesday **September 5**	**09:00-10:30 Talks** 10:00-10:30 Coffee break **10:30-12:30 Talks** 12:30-14:00 Lunch	**14:00-16:00 Talks** 16:00-16:30 Coffee break **16:15-18:00 Posters**	19:00-20:00 Aperitif
Thursday **September 6**	**09:00-10:30 Talks** 10:00-10:30 Coffee break **10:30-12:30 Talks** 12:30-14:00 Lunch	**14:00-15:45 Talks** **15:45-16:15 General discussion** 16:15-16:45 Coffee break **16:45-18:00 Posters**	20:00 Conference dinner
Friday **September 7**	09:00-18:00 Visit to the Monaco Oceanographic Museum (12:30-14:00 lunch at the panoramic restaurant of the Museum)		

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Lists of oral and poster presentations

Program of the conference

Tuesday 4th September 2012

9h00-10h00 Registration of participanats

10h00-10h15 welcoming address

10h15-10h30 commemoration of Michael Ivanov by John Woodside

10h30-11h00 coffee break

11h00-12h30 **session: geophysical and geological expression of gas structures**

conveneers: Jean Mascle and Daniel Praeg

11h00-11h30 **Invited talk: David Scholl**

Scholl D, Wood W, Barth GA, Childs JR: THE BERING SEA BASIN: NEW DRILLING AND GEOPHYSICAL OBSERVATIONS AND EVIDENCE FOR AN IMPORTANT CONTRIBUTION OF THERMOGENIC METHANE TO INTERSTITIAL DEPOSITS OF METHANE HYDRATE

11h30-11h45 **Gafeira J, Long D, Diaz-Doce D** : WHAT CAN WE FOUND OUT FROM THE SEMI-AUTOMATED CHARACTERISATION OF 4150 POCKMARKS WITHIN THE WITCH GROUND BASIN (CENTRAL NORTH SEA)?

11h45-12h00 **Ho S, Imbert P, Cartwright J**: A CASE STUDY OF FLUID VENTING STRUCTURES AND AMPLITUDE ANOMALIES AS INDICATORS HYDROCARBON LEAKAGE IN INTERPLAY WITH GEOLOGICAL SETTING, NEOGENE-QUATERNARY INTERVAL OF LOWER CONGO BASIN

12h00-12h15 **Veloso M, De Batist M, Mienert J, Greinert J** : SPATIAL DISTRIBUTION ANALYSIS AND HYDROACOUSTIC MONITORING OF A GAS SEEP AREA OFFSHORE SVALBARD (~ 78 N)

12h15-12h30 **García-Gil S, Muñoz Sobrino C, Martinez-Carreño N, de Blas E** : SHALLOW GAS AND STRATIGRAPHIC ARCHITECTURE OF THE SEDIMENTARY RECORD FROM AN ENCASED VALLEY: RIA DE VIGO

12h30-14h00 lunch

14h00-15h45 **Session: imaging subseafloor gas structures by seismic studies**

conveneers: Marc De Batist and David Scholl

14h00-14h30 **Invited talk: Jean Mascle**

Mascle J, Mascle G, Camera L, Brosolo L : MUD VOLCANOES AND FLUID SEEPAGE IN THE MEDITERRANEAN DOMAIN

14h30-14h45 **Gafeira S, Long D, Diaz-Doce D** : SEMI-AUTOMATED CHARACTERISATION OF SEABED POCKMARKS FROM MULTIBEAM BATHYMETRIC DATASETS

14h45-15h00 **Wenau S, Spiess V, Fekete N**: SEISMIC AND ACOUSTIC INVESTIGATION OF ACTIVE GAS SEEPAGE SITES CONTROLLED BY SALT TECTONICS IN THE LOWER CONGO BASIN

15h00-15h15 **Klaucke I, Bialas J, Klaeschen D, Zander T, Papenberg C, Dumke I, Koch S** : SUBSURFACE FLUID-FLOW PATTERNS WITHIN THE GAS-HYDRATE STABILITY ZONE OF THE BLACK SEA

15h15-15h30 **Pattier P, Loncke L, Gaullier V, Basile C, Lacoste A, Vendeville BC, Roest WR, Maillard A** : SEAFLOOR FLUID EMISSIONS IN THE FRENCH GUIANA PASSIVE TRANSFORM MARGIN (DEMERARA PLATEAU)

15h30-15h45 **Praeg D, Migeon S, Mascle J, Ketzer J, Augustin AH, Dano A, Diviacco P, Geletti R, Wardell N, Rodrigues LF, Unnitham V** : MULTI-DISCIPLINARY INVESTIGATIONS OF GAS HYDRATES AND FLUID SEEPS ON THE NILE FAN

15h45-16h15 coffee break

16h15-18h00 **Session: seafloor emissions to the water column and the atmosphere**

conveneers: Ingo Klaucke and Soledad Garcia Gil

16h15-16h45 **Invited talk: Louis Géli**

Géli L and Marmara-DM group: SUBMARINE INVESTIGATIONS OF THE SUBMERGED SECTION OF THE NORTH ANATOLIAN FAULT WITHIN THE SEA OF MARMARA OPENS NEW PERSPECTIVES FOR THE DEEP SEAFLOOR MONITORING OF EARTHQUAKE HAZARDS

16h45-17h00 **Hsu SK, Liao YC, Wang SY, Yang TF, Tsai TF, Chen SC**: MECHANISM OF GAS EMISSIONS OFF SW TAIWAN

17h00-17h15 **Egorov AV, Nigmatulin RI, Rimsky-Korsakov NA, Rozhkov AN, Sagalevich AM, Chernyaev ES** : TRANSFORMATION OF DEEP-WATER METHANE BUBBLES INTO HYDRATE POWDER AND HYDRATE FOAM

17h15-17h30 **Dupré S, Scalabrin C, Géli L, Henry P, Grall C, Çagatay N, Imren C and the MARMESONET Scientific Party Team :** WIDESPREAD GAS EMISSIONS IN THE SEA OF MARMARA, RESULTS FROM SYSTEMATIC SHIP-BORNE MULTIBEAM ECHOSOUNDER WATER COLUMN IMAGERIES

17h30-17h45 **Leifer I, Solomon E, Levine J, Kastner M, Rehder G** : DEEP SEEP BUBBLES REACH FOR THE SKIES: GROWING EVIDENCE OF BUBBLE-MEDIATED METHANE/HYDROCARBON TRANSFER FROM DEEP WITHIN THE HYDRATE STABILITY FIELD TO THE ATMOSPHERE

17h45-18h00 **Ulyanova M, Sivkov V, Kanapatskiy T, Pimenov N** : METHANE DIFFUSIVE FLUX IN THE SHALLOW LAGOONS OF THE SE BALTIC SEA

19h00-20h00 ice breaker

Wednesday 5th September 2012

9h00-10h30 **Session: subsurface fluid flow, cold seeps, geochemical and thermal gradients**

conveneers: Jeffrey Poort and Elena Suetnova

9h00-9h30 **Invited talk: Tatiana Pogodaeva**

Pogodaeva T, Zemskaya TI, Khlystov OM : PRELIMINARY ESTIMATE OF DISSOLVED COMPONENTS FLOWING THROUGH WATER-BOTTOM INTERFACE AT SITES OF OIL AND GAS DISCHARGE IN LAKE BAIKAL

9h30-9h45 **Villar-Muñoz L, Behrmann J, Villinger H, Karsten J, Klaeschen D, Diaz-Naveas J** : SPATIAL VARIATION OF THE HEAT FLOW AND BSR ON THE SOUTH-CENTRAL CHILEAN FOREARC

9h45-10h00 **Lavrenova E, Kruglyakova M, Gorbuniv A** : DISTRIBUTION OF LIGHT HYDROCARBONS IN MARINE SEDIMENTS (RESULTS OF REGIONAL STUDIES, SOUTH RUSSIA)

10h00-10h15 **Malakhova T** : METHANE DYNAMICS IN SEVASTOPOL BAY (BLACK SEA)

10h15-10h30 **Imbert P** : GAS IN MARINE SEDIMENTS: WHAT MAKES IT DIFFERENT ?

10h30-11h00 coffee break

11h00-12h30 **session: regional studies on gas and gas hydrate distribution and quantification**

conveneers: Patrice Imbert and José Mogollon

11h00-11h30 **Invited talk: Joerg Bialas**

Bialas J and teams of cruises SO-191 and SO-214 : 3D SEISMIC AND MULTIDISCIPLINARY INVESTIGATIONS OF COLD SEEPS ALONG THE HIKURANGI MARGIN, NORTH ISLAND, NEW ZEALAND

11h30-11h45 **Cancelled presentation**

11h45-12h00 **Matsumoto R, Ochiai H, Tomaru H, Hiromatsu M, Oi T** : FREE GASES IN GAS HYDRATE MOUNDS AS MEASURED BY TDR, JOETSU BASIN, EASTERN MARGIN OF JAPAN SEA

12h00-12h15 **Yang TF, Chuang PC, Chen CW, Chen NC, Lin S, Wang Y, Chung SH, Chen PC** : GAS COMPOSITION OF CORED SEDIMENTS FROM GAS HYDRATE POTENTIAL AREA OFFSHORE SW TAIWAN

12h15-12h30 **Casenave V, Imbert P, Gay A** : THE DISTRIBUTION OF BOTTOM-SIMULATING REFLECTORS IN THE LOWER CONGO BASIN: IMPLICATIONS ON HYDRATES FORMATION PROCESSES AND RELATIONSHIPS WITH DEEPER STRUCTURES

12h30-14h00 lunch

14h00-16h00 **Session: regional studies on gas and gas hydrate distribution and quantification**

conveneers: Ryo Matsumoto and Ewa Burwicz

14h00-14h30 **Invited talk: Hitoshi Shoji**

Shoji H, Takahashi N, Jin YK, Obzhirov A, Baranov B : INTERNATIONAL COLLABORATION EFFORTS OF SUBMARINE GAS HYDRATE STUDIES OFFSHORE SAKHALIN, OKHOTSK SEA

14h30-14h45 **Nengkoda N, Prasetyo I, Suryono S, Amijaya H, Tohidi B** : POTENTIAL RISK IDENTIFICATION FROM GAS HYDRATE PRODUCTION: CASE STUDY INDONESIA

14h45-15h00 **Fukumoto A, Sato T** : STUDY ON MORPHOLOGY OF THE METHANE HYDRATE IN POROUS MEDIA

15h00-15h15 **Chernyavski V** : GAS RELEASE FROM SATURATED FLUID DURING FILTRATION IN A PORE; LABORATORY EXPERIMENT AND IMPLICATION TO NATURAL ENVIRONMENT OF MARINE SEDIMENTS

15h15-15h30 **Suetnova E** : PECULIARITY OF GAS HYDRATE ACCUMULATION HISTORY CAUSED BY DIFFERENCE IN RHEOLOGICAL PROPERTIES OF MARINE SEDIMENTS

15h30-15h45 **Monteys X, Garcia R, Hung P, Evans R, Szpak M, O'Reilly S, Kelleher B, Garcia-Gil S** : ACOUSTIC SEDIMENT CHARACTERIZATION IN NEAR SEABED GAS ENVIRONMENTS AROUND THE IRISH COAST

15h45-16h00 **Presentation of the poster session**

16h00-16h30 coffee break

16h30-18h00 **Poster session**

19h00-20h00 Aperitif

Thursday 6th septembre 2012

9h00-10h30 **Session: gas hydrates modeling, biogeochemical processes**

conveneers: Giovanni Aloisi and Vladimir Chernyavski

9h00-9h30 **Invited talk: Ewa Burwicz**

Burwicz E, Rüpke LH, Wallmann K : A NEW NUMERICAL REACTION-TRANSPORT MODEL OF MARINE GAS HYDRATE DEPOSITS

9h30-9h45 **Sa JH, Lee KH** : INFLUENCE OF HYDROPHOBICITY ON THE PERFORMANCE OF INHIBITORS FOR CARBON DIOXIDE HYDRATE FORMATION

9h45-10h00 **Lin S, Kalmychkov V, Cheng W, Hsu CW, Lim Y, Yang TF, Pogodaeva T** : SULFUR ISOTOPIC VARIATION AND ROLE OF SULFATE IN THE FRESHWATER METHANE RICH LAKE BAIKAL CARBON/SULFUR CYCLING

10h00-10h15 **Mogollón JM, Kasten S** : CONSTRAINING THE METHANE CYCLE THROUGH CARBON ISOTOPE MODELS

10h15-10h30 **De Prunelé A, Ruffine L, Peters CA, Guyader V, Donval JP, Bollinger C, Sultan N, Bohrmann G, Pape T, Géli L, Cauquil E** : GEOCHEMISTRY OF PORE FLUIDS FROM A CLUSTER OF HYDRATE-BEARING POCKMARKS, OFFSHORE NIGERIA

10h30-11h00 coffee break

11h00-12h30 **Session: biogeochemical processes, authigenic carbonates**

conveneers: Sylvie Gaudron and Karine Olu

11h00-11h30 **Invited talk: Ivano Aiello**

Aiello IW, Zabel M, Hinrichs KU, Teske A, Goldhammer T, Elvert M, Heuer S: AN EXPANDED SEAFLOOR IN THE BRINE LAKE OF THE URANIA BASIN: A NEW DEEP-WATER MARINE ENVIRONMENT

11h30-11h45 **Blouet J, Imbert P, Ho S** : MORPHOLOGY VARIATIONS OF METHANOGENIC CARBONATES IN RELATIONSHIP WITH THEIR GENESIS MECHANISMS, VOCONTIAN BASIN, FRANCE: A MULTIDISCIPLINARY STUDY

11h45-12h00 **Capozzi R, Dinelli E, Negri A, Montagna P, Oppo D, Picotti V, Scarponi D, Taviani M** : SHALLOW-WATER HYDROCARBON SEEPAGES IN THE PLEISTOCENE ARGILLE AZZURRE FORMATION: THE CHIMNEYS FIELD OF ENZA RIVER, NORTHERN APENNINES, ITALY

12h00-12h15 **Pierre C, Bayon G, Blanc-Valleron MM, Mascle J, Dupré S** : AUTHIGENIC CARBONATES FROM CHEOPS MUD VOLCANO - MENES CALDERA (NILE DEEP SEA FAN-EASTERN MEDITERRANEAN)

12h15-12h30 **Crémière A, Bayon G, Ponzevera E, Pierre C** : PALEO-ENVIRONMENTAL CONTROLS ON METHANE-DERIVED CARBONATES AUTHIGENESIS IN THE SEA OF MARMARA

12h30-14h00 Lunch

14h00-16h00 **Session: biogeochemical processes, biology, microbiology**

conveneers: Ioanna Bouloubassi and Ivano Aiello

14h00-14h30 **Invited talk: Sébastien Duperron**

Duperron S, Rodrigues C, Cunha M, Olu K, Gaudron S : SYMBIOSES BETWEEN BIVALVES AND CHEMOSYNTHETIC BACTERIA ON EUROPEAN AND AFRICAN MARGINS: SUMMARY AND RECENT PROGRESS

14h30-14h45 **Olu K, Caprais JC, Marcon Y, Ondréas H, De Prunelé A, Ruffine L, Bayon G, and the WACS cruise scientific party** : VARIABILITY OF CHEMOSYNTHETIC ASSEMBLAGES AMONG AND WITHIN POCKMARKS OF GULF OF GUINEA

14h45-15h00 **Gaudron S, Rodrigues C, Maros F, Laming S, Pierre C, Duperron S** : COLONIZATION OF ARTIFICIAL SUBSTRATES (CHEMECOLIS) IN DEEP-SEA EUROPEAN REDUCING HABITATS: BIODIVERSITY, SYMBIOSIS AND GEOLOGICAL FACTORS

15h00-15h15 **Dachnova M, Kruglyakova R, Zheglova T, Mozhegova S, Shevtsova N** : THE EXAMPLE OF HIGH MOLECULAR WEIGHT HYDROCARBONS STUDY BY SURFACE GEOCHEMICAL EXPLORATION WITHIN OFFSHORE AREAS (BLACK SEA, YENISEISK AND KHATANGA GULFS OF ARCTIC SEAS)

15h15-15h30 **Chevalier N, Birgel D, Stadnitskaia A, Taphanel MH, Sinninghe Damsté J, Bouloubassi I** : MICROBIAL METHANE OXIDATION AT COLD SEEP SEDIMENTS FROM THE NORWEGIAN MARGIN AND THE MARMARA SEA

15h30-15h45 **Lomakina AV, Morozov IV, Pogodaeva TV, Zemskaya TI**: STUDY ON DIVERSITY OF BACTERIA PARTICIPATING IN CYCLES OF METHANE AND AMMONIUM AT SITES OF HYDROCARBON DISCHARGE IN LAKE BAIKAL

15h45-16h15 **General discussion- propositions for the location of the next conference GIMS12**

16h15-16h45 coffee break

16h45-18h00 **Poster session**

20h00 Conference dinner at “la Maison du Séminaire”

Friday 7th September 2012

9h00-18h00 Excursion to the Monaco Oceanographic Museum

Geo-Marine Letters, Special Issue

Similar to former GIMS conferences in Vigo, Bremen and Listvaynka, we have the acceptation of the editors of Geo-Marine Letters to publish the contributions of participants to the conference in a Special Issue. More informations will be provided after the conference.

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Oral presentations

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Abstracts of oral presentations
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3D Seismic and Multidisciplinary Investigations of Cold Seeps Along the Hikurangi Margin, North Island, New Zealand

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Gas hydrates are a world-wide observed occurrence of mainly Methane gas bound in solid phase within the sediment column. Speculations about the available Carbon from these sources have changed by numbers of orders but still are expected to be larger than the actual known and available resources from oil and gas (1100 Gt - 3500 Gt[*Marquardt et al.*, 2010; *Pinero et al.*, 2012]) and hence investigations about the potential usage as energy reservoirs are continuing. To enable an environmentally save production from those reservoirs a detailed understanding of the stability field, dynamics and chemical processes of the hydrates are crucial. This holds especially for the unusual but often observed migration of free gas within the stability field of gas hydrates.

Sites with active gas expulsion above gas hydrate containing areas are known from various places in the oceans. Wide spread and large amounts of such “Cold Vents” (Seeps) in connection with a BSR have been mapped and documented from the Hikurangi Margin off the North Island of New Zealand (e.g. [*Faure et al.*, 2006; *Greinert et al.*, 2010; *Henrys et al.*, 2003; *Lewis and Marshall*, 1996]). Recent expeditions with R/V SONNE (SO-191& SO-214) contributed to the actual knowledge of the active and passive seep sites along this accretionary margin (Fig. 1).

∂13C isotopic compositions analysed by[*Campbell et al.*, 2010]implied significant temperature variations or episodes of gas hydrate formation.U/Th age data by [*Liebetrau et al.*, 2010]indicate more than 12000 years lifetime with different stages of activity. Analysis of gas samples confirmed that the majority of the gas is of biological origin. But there are sites were deeper sources and other than pure Methane compositions were indicated [*Faure et al.*, 2006], Kipfer, EAWAG).

2-D seismic images of the feeder channels underneath the seep sites indicate that there are different systems of migration pathways supporting free gas transport through the gas hydrate stability field [*Netzeband et al.*, 2010]. BSRs are visible at the various sites investigated along the margin but are missing underneath the active seeps. Ruptured and distributed strong reflections at BSR level at the root of a chimney, chimneys with internal reflections, and possibly connected feeder systems are suggested from the 2-D seismic data.It is clear that these are three-dimensional structures and major parts of the described features are not imaged by the 2-D lines as they are out of plane. The recently developed GEOMAR 3-D P-Cable multichannel seismic acquisition system was applied to provide 3-D images of the feeder channels and the gas hydrate reservoirs. A 3D data cube recorded at Opouawe Bank, Wairarapa, provides images within a 6.25 m * 6.25 m migrated grid.

Parasound data recorded along the dense network of seismic tracks add the high frequent shallow sediment images to this data set.Water column imaging of corresponding gas flares allow the direct correlation of gas distribution in the seafloor sediments with the expulsion site.Deep towed sub-bottom profiler data were acquired to link the high resolution seismic with the seafloor images from the deep towed sidescan sonar.Comparison with the elder maps indicate if significant changes in seafloor composition occurred during the available observation window of four years.

Morphology variations of methanogenic carbonates in relationship with their genesis mechanisms, Vocontian Basin, France: a multidisciplinary study

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The Aptian outcrop of Gigors (Vocontian Basin) shows a 150 m-thick succession in the Aptian/Albian Marnes Bleues (French for "Blue Marls") Formation in lateral continuity over several hundreds of meters. The formation has an overall coarsening-up character and ends up into sandy shoreface deposits. The muddy lower part shows numerous levels with carbonate concretions of variable sizes and morphologies, which are the subject of this study.

Past stable isotope studies (Rubert, pers. com.) have shown that these carbonates derived from anaerobic oxidation of methane and can therefore be considered as various morphologies of Methane-Derived Authigenic Carbonates (MDAC). The goal of the current study is to analyze in more detail the various types of concretions at the scale of the carbonate body and through a detail analysis on polished slices, thin sections and using geochemical techniques, so as to better constrain their mode of emplacement.

MDAC occur with three main fabrics: tubes, nodules and beds (Fig. 1).

1) Tubes (Fig. 1A, B, D, F): Tubes occur in two populations distinguished on the basis of their diameter: the large tubes have an external diameter ranging from 40 to 60 cm. Their overall predominant orientation is subvertical, but they can show folding. They occur at preferential stratigraphic levels, where they are relatively scattered. Small tubes range in external diameter from 2 to 15 cm, and can occur either isolated like their larger counterparts, or in various types of associations: vertically elongated clusters of tubes in a marly matrix, or in lenses with a high carbonate matrix content. Excavating behind the outcrop surface shows that small tubes are most of the time connected in a complex 3-D lattice, with no preferential orientation.

All Tubes have a well-expressed central conduit, with a diameter ranging from 1 to 3 centimeters. The conduit infill is highly variable from one tube to another and reveals a very complex story of successive cementations and dissolutions.

Slabs made of broken tubes lying in horizontal position and encrusted by oyster-like bivalves are one the contrary filled with only a few early cements and mud similar to the surrounding marls.

2) Nodules (Fig. 1C): Irregular nodules occur in layers defining roughly hemispheric domes *ca*. 1 m in diameter with sharp boundaries

3) Beds (Fig. 1E): The last type of carbonates in the Marnes Bleues Fm. consists of irregular limestone beds with occasional protruding roots (downwards) and "horns" (upward).

One of the first questions addressed in the study was to determine whether the tubes had been emplaced at the seafloor or in the shallow subsurface. The occurrence of broken tubes on erosive surface strongly suggested an initial tube emplacement below the seafloor (Fig. 2). Geochemical stable isotopes analyses in progress should help precise the mode of development of these various types of methane-derived authigenic carbonates and to replace then in an evolutionary scheme, in conjunction with the local basin history.

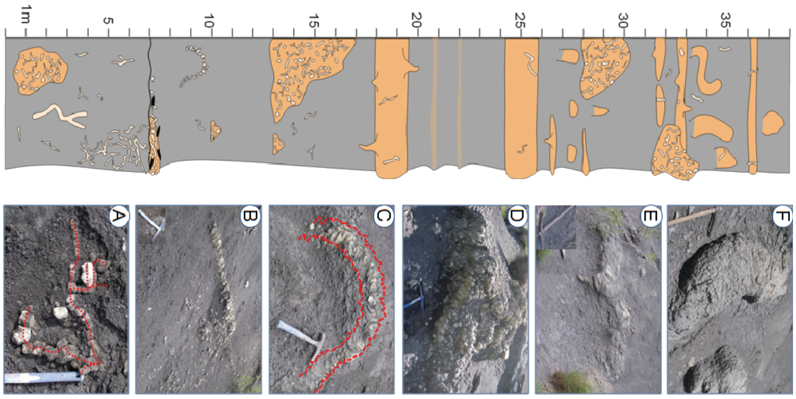

Figure 1 – log of the lower part of the outcrop, showing MDAC diversity. A) Small tube showing complex branching; B) Slab of broken tubes right above a cluster of tube; C) Hemispheric dome made of nodules; D) lenticular cluster of tubes; E) Limestone bed showing a protruding root; F) Large tube.

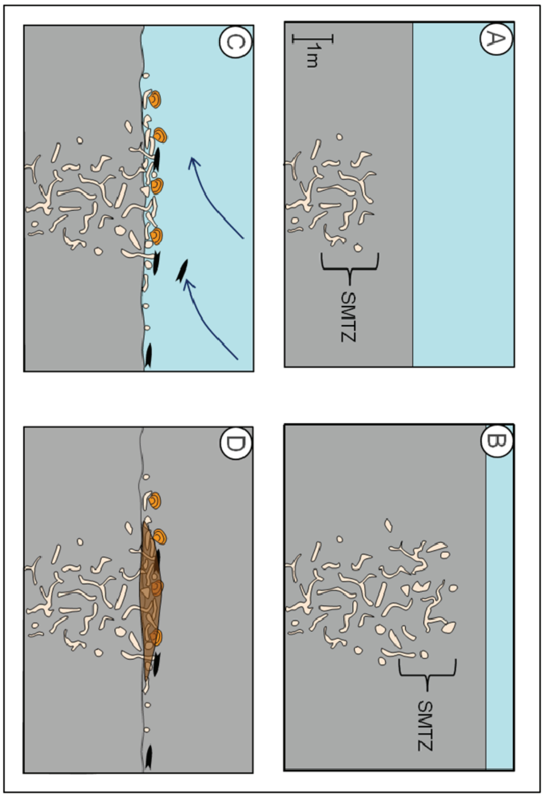

Figure 2 - emplacement of a tube cluster. A) localized hydrocarbon influx inducing tube precipitation in the sulphate-methane transition zone (SMTZ); B) vertical build up of the tube cluster, following the SMTZ rise with sediment accumulation on the sea floor; C) erosive event: tube truncation, belemnite accumulation and encrusting of bivalves on hard substrates; D) resuming of sediment supply and calcareous cementation of the patch of broken tubes.

Remarks:

•Stable isotopic analysis is in progress on calcareous crust shown in D) to investigate its origin.

•thin section analysis on the infill of the broken tubes (in progress) will provide a helpful relative dating tool for the emplacement of early cement.

A NEW NUMERICAL REACTION-TRANSPORT MODEL OF MARINE GAS HYDRATE DEPOSITS

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Introduction

We have developed a new multi 1-D numerical model to investigate and understand theprocesses of gas hydrate formation and dissolution in anoxic marine sediments under a wide range of conditions. By this reaction-transport model we are able to investigate a various aspects of gas hydrate dynamics: sediment compaction which results in expulsion of pore fluids containing various chemical species, reduction in porosity and permeability of the sédiment matrix due to hydrate formation, time-resolved evolution of pressure and temperature regimes, multiphase flow of compressible pore fluids, gas hydrate, and a free gas, thermal-blanketing effect due to vigorous sedimentation of cold impermeable layers, gas hydrate dissolution as a response to a slowing down sedimentation, and the effects of salinity variations on the thickness of the Gas Hydrate Stability Zone (GHSZ).

Numerical model

The reaction-transport model contains various chemical compounds (solid organic carbon, dissolved in pore water methane, dissolved inorganic carbon, dissolved sulfates, gas hydrates, and free methane gas). We consider a reference frame which extends from the seafloor to the bottom of the GHSZ (defined as a combination of pressure, temperature, and salinity conditions) plus 50m of Free Gas Zone lying directly beneath. However, the upper part of sediment column (10 cm) is not considered in the model due to strong bioturbation processes which might potentially have an impact on the gradients of dissolved chemical species.
Initially, the system is filled by compressible pore fluids of a given salinity (consistent with a value at the sediment-water interface). As the upper boundary conditions, we have applied constant concentrations of dissolved methane, dissolved inorganic carbon, and sulfate according to the mean values in the ocean.
At the beginning of each time-step, a new sediment layer is deposited at the top of sediment column according to a given sedimentation rate, lithological type, and initial porosity at the surface.
Transport processes have been split into the advection and diffusion part and solved separately for every chemical compound. Multiphase flow of dissolved chemical species and free gas phase has been solved by finite-volumes method according to the Darcy's law. Molecular diffusion of dissolved species is controlled by changes in concentration gradients and has been solved by finite-elements method.
Reaction module contains kinetically controlled rates of methanogenesis, sulfate reduction, methane oxidation, and POC degradation. POC decay via microbial sulfate reduction takes place until the dissolved sulfate pool in ambient pore waters is depleted. Below the sulfate penetrationdepth, POC is microbially decomposed into methane and CO2. Upward diffusing dissolved methane is consumed by anaerobic oxidation within the sulfate-methane transition zone. This reaction module has been evaluated previously by Wallmann et al., 2006, Marquardt et al., 2010, and Burwicz et al., 2011.

Applications

Dynamic un-steady state compaction allows us to investigate gas hydrate formation and dissolution in terms of changing parameters (e.g. sedimentation rate or permeability of deposited sediments). By depositing sediment layers of a different grain size ('sandwich-like' scenario), we have observed that lithology of potential hydrate-bearing layers (e.g. coarse-grained sands vs. shales) results in preferential hydrate accumulation in the first ones which stays in agreement with field observations.

We have also investigated the effect of slowing down sedimentation rates on gas hydrate dissolution. We have concluded that slow deposition of sediment layers at the top of sediment column and, as a result, a decrease in POC input in time, result in undersaturated in CH_4 pore waters causing hydrate destabilization. This scenario clearly shows the importance of constraining a time-resolved sedimentation history in gas hydrate simulations which are coupled with climate models.

By depositing thick layers of cold low-permeable sediments on top of the column, we have investigated the temperature variations within sediments, known as 'thermal blanketing' effect, which has an impact on previously formed hydrates.

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SHALLOW-WATER HYDROCARBON SEEPAGES IN THE PLEISTOCENE ARGILLE AZZURRE FORMATION: THE CHIMNEYS FIELD OF ENZA RIVER, NORTHERN APENNINES, ITALY

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The geologically young Northern Apennines contain various traces of hydrocarbon seepages, which are linked to fluid migration triggered by the tectonic evolution of the chain and the foredeep. The most known examples, related to comparatively deep water conditions (> 300 m) are clustered in the late Miocene and early-middle Pliocene successions of the region, while their occurrence in shallow water (shelf) settings is very rarely reported. A case in point is represented by the palisade chimneys field recently exhumed along the Enza river banks in the Northern Apennines (Reggio province). Here, a number of modally vertical, metric-high columnar chimneys ranging in diameter from 10 to 35 cm, affect the Argille Azzurre Fm, biostratigraphically dated at the Early Pleistocene (nannoplancton zone NN19). Such columnar concretions are clearly formed by the moderate cementation of the pelitic sediments. Macropaleontological content (mainly bivalves) documents that this unit was deposited in an open marine muddy shelfal setting in a bathymetry range of about 50-70 m. Within the Enza river Argille Azzurre succession some biogenic gas leakages still occur. Preliminary studies suggest that the methane migration can be related to the geologic setting of the foothills in this area, which shows a gentle compressive deformation. On the contrary, numerous hydrocarbon seepages along the northern Apennines foothills are characterized by thermogenic methane generated at depth and presently trapped within Tertiary reservoirs. This suggests to take into account the different geologic context as the main control on gas generation and migration.
The on-going research is focused upon the petrographic, geochemical and biomaker characteristics of these chimneys to unravel the typology of fluids involved in their formation, their concretioning modality and the fluid expulsion history.

THE DISTRIBUTION OF BOTTOM-SIMULATING REFLECTORS IN THE LOWER CONGO BASIN: IMPLICATIONS ON HYDRATES FORMATION PROCESSES AND RELATIONSHIPS WITH DEEPER STRUCTURES (oral presentation)

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The Lower Congo Basin, offshore Angola, is a prolific oil and gas area. Besides the actual presence of commercial accumulations that have been produced for over a decade, evidence of fluid leakage and gas migration is pervasive. Analysis of 3D seismic data, with various resolutions, revealed evidence of fluid flow, including: (1) local Bottom-Simulating Reflectors (BSRs) interpreted as indicators of the base of the hydrate stability zone (GHZS), (2) small mounds interpreted as methane-derived authigenic carbonates, (3) abundant pockmarks, etc. Such objects are identified as present-day features by oceanographic campaigns and are also recognized in subsurface, indicating past activity of the system.

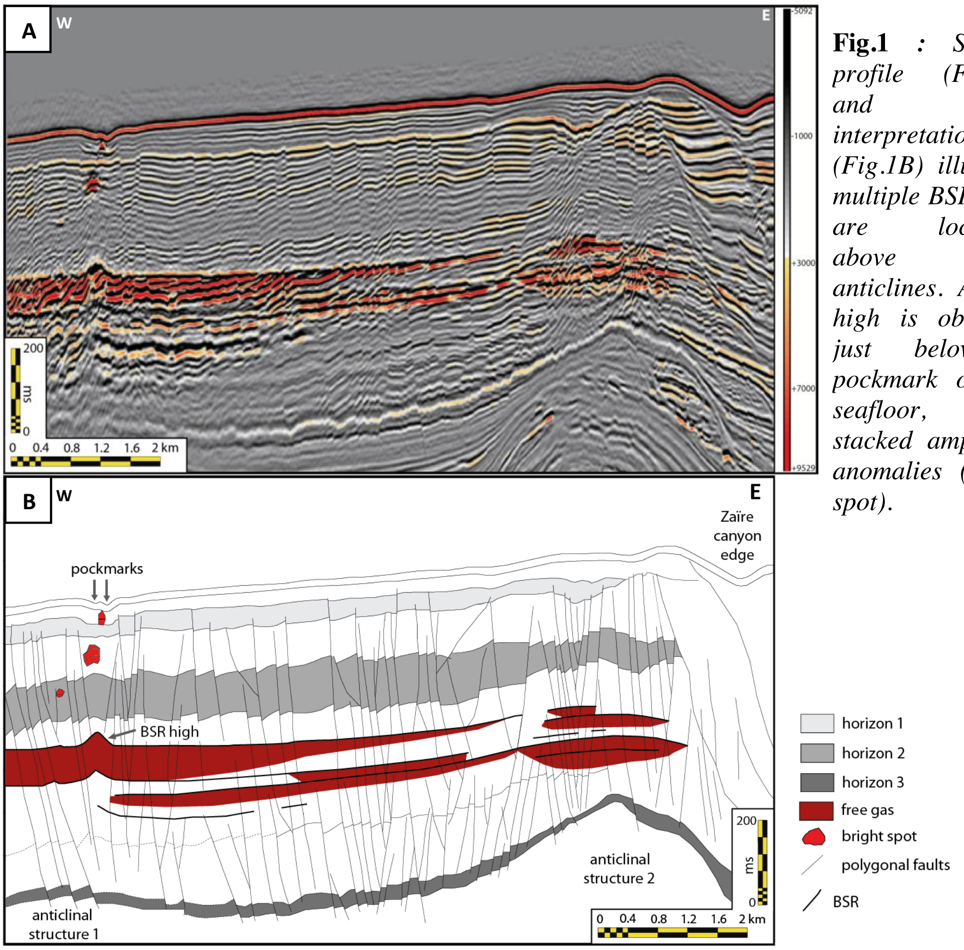

Fig.1 *: Seismic profile (Fig.1A) and its interpretation (Fig.1B) illustrate multiple BSRs that are localized above deep anticlines. A BSR high is observed just below a pockmark on the seafloor, and stacked amplitude anomalies (bright spot).*

In particular, the area of interest, covering a surface of ca. 2500 km², shows several patches of bottom-simulating reflectors, typically within a few hundred meters of the seafloor. The Plio-Pleistocene interval is also affected by numerous normal faults forming a polygonal fault system (*Cartwright et al., 1998*) which may have a relationship with BSRs formation (**Fig.1**).

On a regional scale, BSRs reveal a heterogeneous spatial distribution and develop mostly in the upper part of the area, over approximately 1 000 km². BSRs are almost continuous where the water depth is less than 2000 m, with local holes. In areas deeper than 2000 m, they essentially develop above anticlines (**Fig.1&2**). In most cases, the BSR marks the top of a zone of enhanced reflectivity, several hundreds of ms TWT thick, which is interpreted as free gas-bearing sediments (**Fig.1**).

The depth of the BSR allows evaluating the regional geothermal gradient, as well as its local variation. In particular, local BSR highs are observed just below pockmarks located at the top of stacked amplitude anomalies (**Fig.1**). These local highs have a diameter of a few hundreds of meters. In that case, they are interpreted to result from a change in thermodynamic conditions, such as circulation of warm fluids from deeper down the section. Another BSR anomaly is observed on the top of a faulted anticline. The depth of this BSR is different on the two sides of a normal fault (**Fig.2**). This shift is probably due to different thermal regimes on each fault compartment. These two phenomena show the active character of gas migration in these local gas flow structures. In addition, about 15 % of the area with BSR shows evidence of multiple BSRs, with up to five distinct parallel reflectors, that are not regularly spaced (**Fig.1**). Such multiple occurrences may be related to changes in (P, T) conditions over time possibly due to sea-level fluctuations, or to variable fluid composition (methane, CO_2, etc)

Put all together, these various observations on local variations of BSR depth should lead to a better understanding, and possibly quantification, of gas flux and its evolution through time, in particular in relation with sea-level changes. This is one of the objectives of a PhD work about seismic indicators of fluid migration in the basin, which started in July 2012.

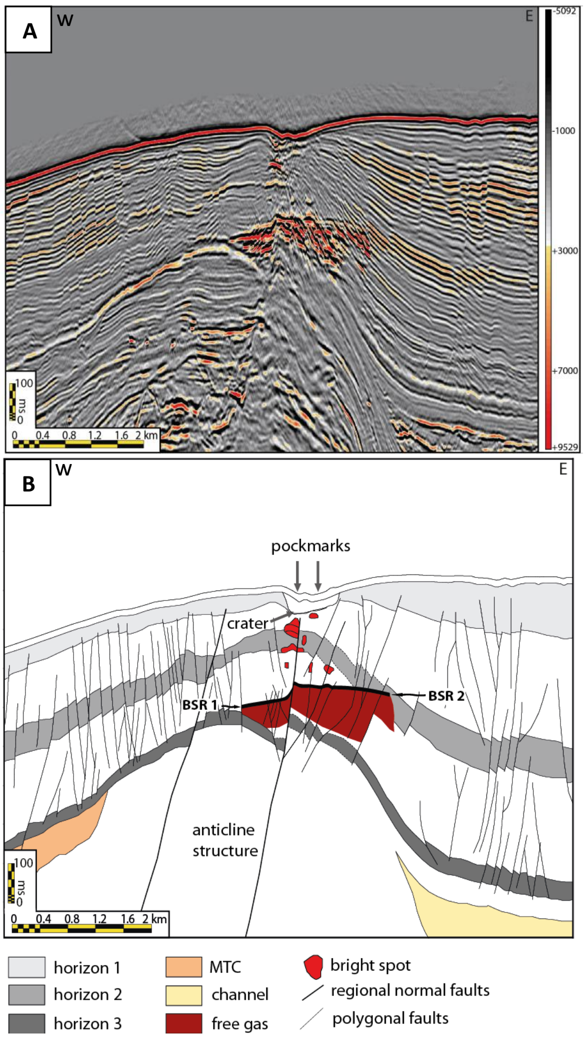

Fig.2 *: Seismic profile (Fig.2.A) and its interpretation (Fig.1.B) illustrate local BSR above an anticline structure which surmount a zone of enhanced reflectivity. A shift of the BSR is observed between the two compartments of a normal fault.*

GAS RELEASE FROM SATURATED FLUID DURING FILTRATION IN A PORE; LABORATORY EXPERIMENT AND IMPLICATION TO NATURAL ENVIRONMENT OF MARINE SEDIMENTS

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During geological history of marine sediments the filtration of porous fluid upward is a basic process which governed by sediments compaction. Geochemical processes in sediments lead to saturation of the pore fluid by the gases. The release of free gas from saturated fluid should take place if local thermodynamic equilibrium in solution is disturbed (Davie, Zatsepina and Buffet 2004). Such disturbances are related to change of a pressure-temperature condition of filtration. In present study the release of free gas in pore during filtration have been investigated on the base of appropriate laboratory experiments. The set of experiment of gas-saturated fluid filtration in artificial porous medium have been done to simulate the process of gas release and trapping throughout the process of upward filtration in marine sediments.

The hydrodynamic experiments allow to see how saturated fluid flows through pore under applied pressure. Changing the local fluid pressure near the throat due to hydrodynamic factors are similar to those previously established for the movement of the contact line (Chernyavski V. Monachov A., 2010) Such a local change leads to liberation of some volume of free gas corresponding to solubility conditions. The classical mathematical formulation of the problem requires the continuity of the liquid. A number of examples indicate that this formulation leads to results that are contrary to physical experience. Various hypotheses were expressed about the reason for the paradoxical behavior of the theoretical solutions. At present the experimental results found that, under certain circumstances, creeping flow may contain gas-vapor bubbles, which arise due to rupture of the liquid.

Recorded the formation of cavitations bubbles in the fluid motion in an experimental device are simulating the output throat of a single pore. The theory, in turn, shows that the flow contains the area with large negative pressures greater than the tensile strength of the liquid. Localization of low pressure is close to that observed in the experimental location of bubbles.

The results of experimental studying show that gas can be trapped near pore throat due to local pressure change in pore. This local pressure change depends on the decreasing of throat radius relatively to radius of pore and applied pressure. Thus, the results show that a certain amount of free gas may be formed in the pores during the filtration of fluid.

The work was supported by RFBR grants 11-08-01061-a, 10-05-01094-a.

MICROBIAL METHANE OXIDATION AT COLD SEEP SEDIMENTS FROM THE NORWEGIAN MARGIN AND THE MARMARA SEA

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Aiming at gaining further insight into microbial processes of methane cycling and the microbial communities involved,we investigated diagnostic lipids and their carbon isotope composition at two methane seepage areas in European seas with distinct geological features.

On the mid-Norwegian margin, we focused on cold seeps in the Nyegga pockmark field explored during the VICKING cruise (2006) in the framework of the HERMES project. In the Marmara Sea, a tectonically active area located on the North Anatolian Fault, we investigated sites of active fluid venting along the faults, discovered and explored during the MARNAUT cruise (2007). Sediment cores were retrieved during submersible dives at sites with distinct benthic communities (microbial mats, polychaetes, gastropods...).

The studied sediment cores contained abundant and strongly ^{13}C-depleted archaeal lipids (δ^{13}C values as low as −136‰), consisted mainly of archaeol, *sn*-2-hydroxyarchaeol, crocetane and unsaturated PMIs. Concurrently, bacterial lipids (e.g. cyclopropyl-$C_{17:0}$, $C_{16:1\omega5}$, *i-*/*ai*-$C_{15:0}$, and non-isoprenoidal glycerol ethers) were identified with very low δ^{13}C values (down to −115‰). These lipid biomarker patterns indicate the presence of anaerobic oxidation of methane (AOM) associated with sulphate reduction (SR) mediated by methanotrophic archaea (ANME) and sulphate reducing bacteria (SRB). The depth profiles of AOM-lipids reveal distinct vertical zonation of the AOM/SRB process controlled by fluid flow rates and, possibly, by bioirrigation activities of benthic animals.

The composition patterns of lipids indicated that at both sites ANME-2 archaea and *Desulfosarcina*/*Desulfococcus* SRBare the dominant assemblages. However, a number of discrepancies in the lipid composition and/or isotope signature, as well as the identification of a new, strongly ^{13}C-depleted compound (tricosadiene), suggest the presence of multiple ANME/SRB assemblages or contributions from methane-depended microbial species not yet characterised.

Our data sets expand on existing observations and knowledge of AOM at methane seepage areas and highlight similarities/differences between various cold seeps on the European margin.

PALEO-ENVIRONMENTAL CONTROLS ON METHANE-DERIVED CARBONATES AUTHIGENESIS IN THE SEA OF MARMARA

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The factors controlling fluid emission dynamics at ocean margins are poorly understood. In particular, there are significant uncertainties on how fluid seepage at cold seeps may have responded to abrupt environmental changes in the geological past. In this study, we report on a detailed geochemical investigation of seafloor carbonate crusts sampled by manned submersible at cold seeps along the submerged part of the North Anatolian Fault system in the Sea of Marmara - an inland sea, which has experienced major paleo-environmental changes since the last deglaciation period. We also analysed a series of authigenic carbonate concretions recovered from two sediment cores at the Western-High ridge, an active deep-sourced fluid venting area.

The seafloor carbonate pavements exhibit a wide range of stable carbon and oxygen isotopic compositions, which reflect the diversity of fluid sources and biogeochemical processes in the Marmara basin. The carbonate ages derived from isochron U-Th dating cover the last 6 kyr, suggesting that fluid venting activity along the fault system remained probably continuous over that time interval. In the sediment cores, abundant carbonate concretions were found in the lacustrine-to-marine transition, which corresponds to the period when Mediterranean waters flowed into the Sea (lake) of Marmara, about 12-14 kyr ago. Interestingly, U-Th isotopic data indicate that most of these concretions formed later during the Holocene, around 8-11 kyr ago, a period coinciding with an important anoxic event that led to the deposition of sapropel in the Sea of Marmara.

Based upon these results, we propose that the absence of carbonate concretions in the lacustrine sediment unit, deposited before the last marine transgression, reflects that dissolved sulphate concentrations at that time were presumably too low to promote significant methane turnover at seepage sites, thereby preventing carbonate authigenesis. Most probably, the progressive incursion of Mediterranean waters into the Marmara basin after 13 ka led to much higher hydrocarbon consumption rates at seepage sites, through providing sustained influx of dissolved sulphate. Importantly, the contemporaneity between the main phase of authigenic carbonate precipitation at the studied sites (average 9.4 ± 1.8 ka, n=16) and the regional anoxic sapropel event suggests that the drop in bottom water dissolved O_2 content was also a key factor to enhance microbial activity and associated carbonate precipitation at that time. Overall, our results clearly show that fluid emission dynamics and hydrocarbon oxidation at cold seeps can be directly related to changing environmental conditions through time.

The example of high molecular weight hydrocarbons study by Surface Geochemical Exploration within offshore areas (Black Sea, Yeniseisk and Khatanga Gulfs of Arctik Seas)

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With the appearance of the high-sensitivity analytical technics, allowing to detect hydrocarbons at their very low concentration in the sediments by Surface Geochemical Exploration along with gas survey, high-molecular hydrocarbons (HMH) began to be studied. Possibility of use of geochemistry of HMH with the prospecting purposes is caused by that their structure and distribution in immature organics of recent sediments radically differ from those in mature parent rocks and in oil and gas deposits.

Complex of HMH study in the sediments includes Total Scanning Fluorescence (TSF), Gas Chromatography (GC) and Gas Chromatography – Mass Spectrometry (GC-MS). TSF method states a semiquantitative estimation of the content of typical for oils aromatic hydrocarbons in the sediments (the presence of migrated mature hydrocarbons). GC and GC-MS methods allow to identify the hydrocarbons migrating from mature parent rocks or deposits on specificity of their structure and distribution. Information content of methods is considered on an example of research of bottom sediments of the Black Sea, the Yenisei and Khatanga gulfs of the Arctic Seas.

Black Sea. Study of extracts of sediments from the Manganari volcano where oil show are found out and from the sediments outside of a volcano have shown contrast differences between them on all indicators of composition of high-molecular hydrocarbons (HMH). All extracts from sediments from the volcano are characterized by high intensity of fluorescence (TSF). Geochemical researches show that hydrocarbons of oil seeps have undergone strong by bacterial attack to what the big "humps" corresponding to a complex mixture of undivided compositions (UCM) testify (fig. 1 a). Such type of chromatogramms is peculiar to extracts from the recent sediments containing hydrocarbons migrating from depth, undergone to microbiological oxidation. On the chromatogramm of an extract from background samples only high-molecular n-alkanes (n-C25 – n-C33) are presented in the structure of which odd homologues (fig. 1 b) are dominated.

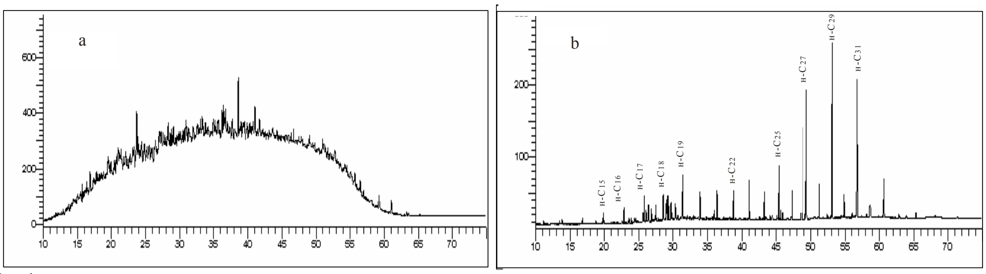

Fig 1. . Gas chromatograms of extracts from the sediments of the Black Sea (a- oil seeps on Manganari volcano, b – the sediment outside of the volcano)

According to GC-MS analysis distribution of triterpanes in extracts from the volcano sediments has a "mature" almost oil shape, hopanes with a "geological" configuration are dominated (fig. 2a). The relative content of "biological" hopanoids and moretans with an intermediate configuration is the lowest. In the structure of triterpanes samples outside of a volcano "biological" hopanoids and moretans are obviously prevail (fig. 2б). GC-MS analysis of oil seeps on the Manganari volcano has allowed us not only to confirm the presence of migrating with

~~depth~~ thermogenic hydrocarbons, but also to determine characteristics of parent thicknesses generating them [1]

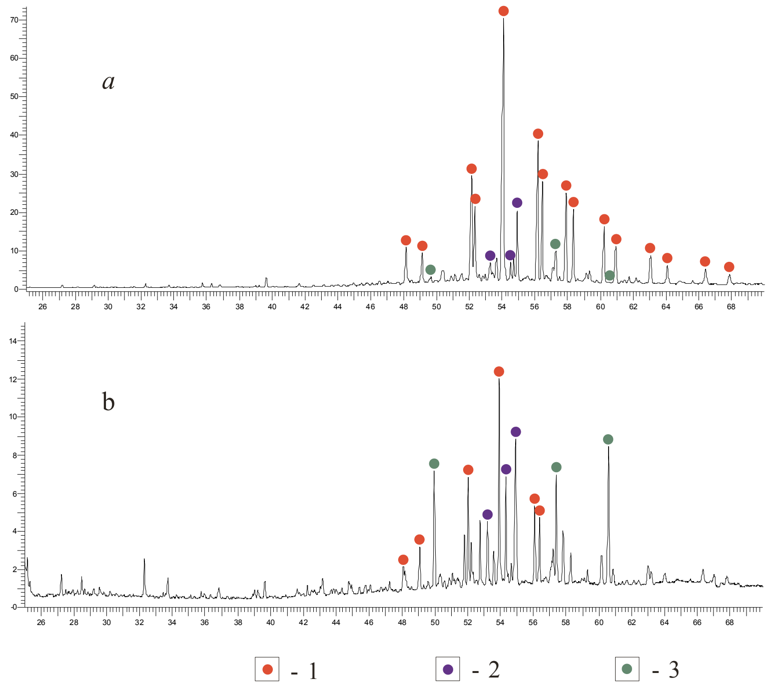

Fig.2. Typical mass - fragmentograms of triterpanes (m/z 191) of extracts from the sediments of Manganari volcano (a) and the sediment outside of the volcano (b)
1 - hopanes with "geological" 17 ά ().21ß (H) – configuration; 2 - moretans with labile intermediate 17 ά (H).21ß (H) – configuration; 3 – hopanoids with astable "biological" 17 ά (H).21ß (H) - configuration

The Yenisei gulf of Kara Sea. On the 10th Conference «Gas in Marine Sediments» on Baikal the results of gas-geochemical researches of gulfs sediments of the Arctic Seas are given [2]. In gulf sediments at three stations shows of liquid hydrocarbon-fluids, on one – a gas seep are fixed. Indications of possible presence of therrnogenic hydrocarbons is revealed according to TSF method (fig. 3a); to size of relation S1/Corg and on character of alkanes (n-paraffins) distribution. Four local areas with abnormal high geochemical indicators are found.

GEOCHEMISTRY OF PORE FLUIDS FROM A CLUSTER OF HYDRATE-BEARING POCKMARKS, OFFSHORE NIGERIA

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On continental margins fluids including light hydrocarbons migrate through the sediment column from greater depth and escape into the water column at cold seeps. In case of relatively intense fluid circulation and expulsion, such seeps are often associated with craterlike seafloor depressions, broadly defined as pockmarks. Usually, methane is the major component of the gas which is influencing the biogeochemistry at the emission sites.

The Niger delta, an area characterized by a high number of pockmarks, has been investigated in detail in recent years. Bathymetric surveys showed pockmarks with diameters ranging from few tens to several hundreds of meters. Seismic surveys and groundtruthing by gravity corer performed in the frame of two cruises, NERIS (2004) and ERIG 3D (2008), indicated the presence of shallow gas hydrates at several of those pockmarks (e.g. Sultan et al, 2010).

During the French-German Guineco-MeBo cruise with RV 'Pourquoi Pas?' (November-December 2011), a joined collaboration between IFREMER and MARUM, selected pockmarks has been investigated. The study focused on a cluster of three hydrate-bearing pockmarks with diameters from ~ 500m to 800m at a water depth of approx 1150m. For the recovery of sediment cores for analyses, four sampling tools including the sea floor drill rig MeBo, the Dynamic Autoclave Piston Corer, and a gravity corer (all from MARUM) as well as the Calypso corer from IFREMER have been deployed. From all these cores pore waters, sediments, and gas hydrates when present were collected for geochemical analyses.

Here, we present a geochemical study, which was performed to contribute to the understanding of fluid circulations at pockmarks and to better constrain the factors controlling gas hydrate formation. Pore fluids from eight Calypso cores collected at different pockmark locations have been sampled using Rhizon samplers. The pore water samples were stored in pre-evacuated and sealed vials until at the laboratory at IFREMER.

The vertical pore water profiles show different burial depths of the Sulfate-Methane-Interface (SMI), with the SMI being located close to the sediment surface (~ 5m below seafloor) in the centre of the pockmark and much deeper outside (> 15m below seafloor). The sulfate profiles suggest that the anaerobic oxidation of methane is the dominant sulfate reducing process. In the course of this process HCO_3^- is released and promotes the precipitation of authigenic carbonates.

Negative pore water chloride anomalies indicate that gas hydrates were recovered with one core (e.g Bohrmann and Torres, 2006). For all other cores, the overall presence of sulfate indicated that neither the SMI nor hydrate layers have been penetrated. Analyses of major dissolved elements (Cl^-, SO_4^{2-}, Br^-, Ca^{2+}, Mg^{2+}, K^+, Na^+), methane, and minor dissolved elements (Li+, B^{4+}, Ba2+, Sr^{2+}, Si^{4+}, Mn^{2+}, Fe^{2+}) are in progress and will be discussed during the conference.

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SYMBIOSES BETWEEN BIVALVES AND CHEMOSYNTHETIC BACTERIA ON EUROPEAN AND AFRICAN MARGINS: SUMMARY AND RECENT PROGRESS

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Bivalves are among the dominant fauna occurring at deep-sea cold seeps, hydrothermal vents and organic falls worldwide. This is due to their ability to establish symbioses with sulphur- and methane-oxidising bacteria,which produce complex organic matter that feeds their hosts. Until recently very little data was available regarding bivalve symbioses in the eastern Atlantic and Mediterranean, but thanks to recent international programs, this gap in our knowledge is currently being filled. In this presentation we present and summarize data regarding symbioses in more than 20 species belonging to families Mytilidae, Vesicomyidae, Thyasiridae, and Lucinidae. This includes host and symbiont diversity, morphology, symbiont functioning and acquisition. We then compare with symbioses documented in western Atlantic and Gulf of Mexico bivalves, and discuss morphological, geographical, and evolutionary trends. In particular, strong connectivity has been suggested between metazoan populations from both sides of the Atlantic in several species (the Atlantic Equatorial Belt, AEB, hypothesis). Whether this also applies to bacterial symbionts remain to be tested. Indeed, symbiont acquisition is different among the different bivalve families, and reservoirs of free-living forms of the symbionts probably exist. Based on new data, we evaluate the AEB hypothesis for bacterial symbionts.

WIDESPREAD GAS EMISSIONS IN THE SEA OF MARMARA, RESULTS FROM SYSTEMATIC SHIP-BORNE MULTIBEAM ECHOSOUNDER WATER COLUMN IMAGERIES

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The number of seep areas identified on the sea bottom has been constantly increasing with the use of multi-scale imagery techniques. Until recently, acoustics in marine geosciences have been mostly used to explore the seabed and image sub-bottom units, with little attention to the water column. The Sea of Marmara located on the transform plate boundary between the Eurasian and Anatolian plates is characterized by an intense seismic activity causing catastrophic earthquakes. The understanding of the evolution of the fluid-fault coupling processes during the earthquake cycle is a challenge and the acoustic detection of gas emissions through the seabed may provide new insights on these processes. Fluid escapes are known to occur at the seabed in the Sea of Marmara. The primary goals of the conducted study were to 1) establish an accurate spatial distribution of the seeps at the scale of the entire sea and 2) investigate the relationship with the fault network and the sedimentary environment. Shipborne multibeam surveys of the water column were conducted there for the first time during the MARMESONET expedition in 2009. Data were acquired with a Simrad EM302 echosounder and analysed with the Sonarscope software (© Ifremer). Gas bubble echoes were very well detected within the entire water depth range. The distribution of water column acoustic echoes reveals that free gas emissions from the seabed are widespread. Numerous acoustic gas flares were detected in association with the North Anatolian fault system. However, gas emissions also spread around the edges of the sedimentary basins (e.g. Cinarcik and Tekirdag basins) and on structural highs (e.g. Western and Central highs).

TRANSFORMATION OF DEEP-WATER METHANE BUBBLES INTO HYDRATE POWDER AND HYDRATE FOAM

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During the Russian Academy of Sciences "MIRI na Baikale, 2008–2010" expedition, deep-water experiments with the bubbles of methane seeping from the bottom at depths 405, 860 and 1400 meters were carried out. These depths correspond to gas hydrate stability zone. Bubbles were caught by the trap which was looked like an inverted glass. It was found that the behavior of bubbles in a trap depends on the depth. At depth of 405 meters formation of hydrates was not observed. Having got to a trap at the depth of 860 meters, bubbles became covered by solid hydrate envelope, kept the initial form, and after a time period collapsed in a number of hydrate fragments which showed all properties of a granular matter. No visible changes in the hydrate granular matter were observed in the course of lifting it to a depth of 380 meters. Shallower, the decomposition of the hydrate granular matter into methane gas was observed. In the experiments at depth of 1400 meters the caught bubbles, becoming covered by hydrate envelope formed solid hydrate foam in the trap. At lifting this foam structure was deformed slightly but simultaneously a free gas left the foam and filled the trap. The volume of free gas in the trap at lifting varied according to the Boyle-Mariotte law.

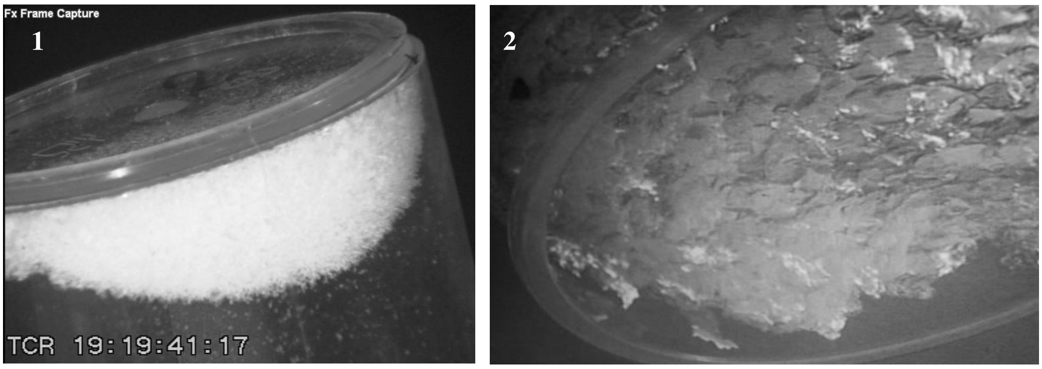

Figure.
Close up of: 1 - granular gas hydrate substance like a powder (860 m), 2 - the bottom of the trap filled with rigid gas hydrate foam (1400 m). Diameter of the trap is about 10 cm.

The observed phase transformations proceeding in methane bubbles are capable of considerably impacting the exploitation of deep-water constructions. This was clearly demonstrated during the recovery efforts following the accident of April 20, 2010, at the Deepwater Horizon oil production platform in the Gulf of Mexico. The attempt to mount a 100-ton submarine bell above the oil escape site resulted in the fact that the bubbles of the oil-associated gas formed a gas hydrate plug preventing the oil removing from the bell. These difficulties forced the BP administration to abandon the idea of bell usage. According to the results of the present study, the problems with the bell usage were caused by its deployment at the depth of 1520 m, which is unfavorable for this technology. This depth is close to that of our surveys at the deep-water St. Petersburg mud volcano (1400 m), where the transformation of methane bubbles into a stable solid hydrate foam was observed. If the bell had been installed at a shallower depth, e.g., at 860 m, the methane bubbles, like those at the Gorevoi Utes test area, would most probably have transformed into a granular substance that can be easily removed together with the oil.

Evidently, the discovered effects might occur not only in the course of underwater drilling but also during the exploitation of submerged pipelines and cables. Thus, knowledge of the mechanics of the phase transformations of deep-water methane bubbles is of substantial importance for the optimal and safe selection of a specific technology for deep-water works in the waters of the World Ocean.

This study was supported by Program no. 23, 27 of Basic Research of the Presidium of the Russian Academy of Sciences, by the Foundation for the Assistance of Lake Baikal's Preservation, and by Government Contract no. 16.420.11.0013.

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STUDY ON MORPHOLOGY OF THE METHANE HYDRATE IN POROUS MEDIA

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Since reformation of hydrate may block gas-water two-phase flow in sub-seabed sand sediments during the methane production from gas hydrate, it is important to know how it forms in the sediment to design a safe and efficient process for the production. In this study, we calculated the morphology of methane hydrate in porous media by using the phase-field model, tacking account of mass and heat transfer. Starting points of hydrate growth are determined by the fluctuation of energy in water, which is derived from the Brownian motion. The presence of foreign substances is considered by using the idea of the classical nucleation model of heterogeneous nucleation.

Acknowledgements: This research was entrusted by the Ministry of Economy, Trade and Industry of Japan and the MH21 Research Consortium, as a part of the research for production method and modelling of methane hydrate.

WHAT CAN WE FOUND OUT FROM THE SEMI-AUTOMATED CHARACTERISATION OF 4150 POCKMARKS WITHIN THE WITCH GROUND BASIN (CENTRAL NORTH SEA)?

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Pockmarks were first discovered within the UK waters in 1970 during a rig site survey in the Forties Field in the North Sea. Since then pockmarks have been found within lakes and estuaries, on the continental shelf and in deeper waters. However the area of the North Sea where the first pockmarks were discovered, the Witch Ground Basin, is still considered the primary location of pockmarks on the UK waters. This extensive area in the central North Sea, where the seabed comprises a thick sequence of muds and sandy muds of the late glacial Witch Ground Formation, shows numerous inactive pockmarks, typically 20-100 m diameter and 3-4 m deep. A few larger, active pockmarks, 500 m diameter and up to 17 m deep are also known.

The vast number of pockmarks and the existence of several high-resolution multibeam data sets made this area a prefect case study for testing a recently developed semi-automated method of mapping and morphometric characterization of vast number pockmarks at seabed. Almost 4150 pockmarks were mapped applying this method to 18 selected site surveys across the study area (Fig.1), providing the outline and location of deepest point of each the pockmark, plus there individual: area, perimeter, area/perimeter ratio, depth, maximum water depth, minimum water depth, maximum slope, mean slope, azimuth and major axis length. Additional information was also derived from the extracted morphologic characteristics, such as the pockmark eccentricity.

This vast amount of information allowed the identification of certain trends within and intersite surveys. Little variation in the depth of pockmark was found with water depth (Table I). However, the density of pockmarks decreases from nearly 30/km2 in the centre of the basin where water depths exceed 150 m, the soft sediments of the With Ground Formation are 20-30 m thick and the surface sediment is mud, to less than 5/km2 on the edge of the basin where water depths are around 120 m, the Witch Ground Formation is less than 10 m thick and the seafloor sediment is muddy sand / sandy mud. The pockmarks show consistent eccentricity that reflects the bottom water currents recorded on recent current meters, varying from NNE-SSW in the east of the study area to NNW-SSE in the west and north. This may imply that the modern current regime has been active for a long period of time.

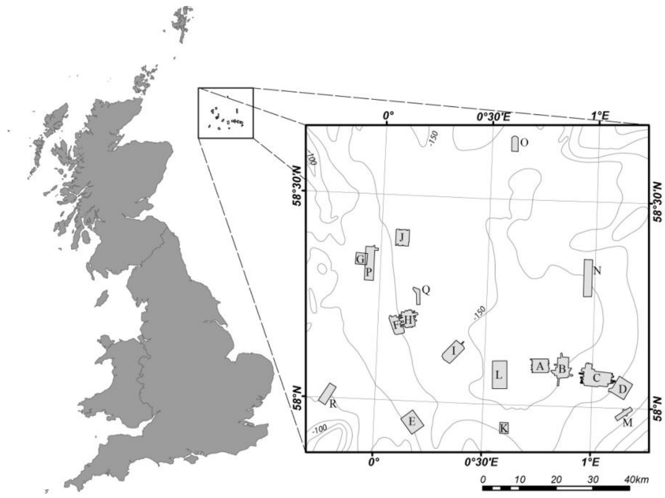

Figure 1 - Location map of the 18 multibeam data sets used during this study.

Table I - Table with the results obtains for each study area, presenting the number of pockmarks delineated, pockmark density (no of pockmarks per km2), area of the biggest pockmark, the average pockmark area, the maximum pockmark depth and the average pockmark depth.

Study Area		Nº of pockmarks	Pockmark density	Maximum Pockmark Area (m^2)	Average Pockmark Area (m^2)	Maximum Pockmark Depth (m)	Average Pockmark Depth (m)
A	Britannia A	355	20.98	55902	4462	5.57	2.10
B	Britannia B	382	17.56	15795	3623	4.99	1.74
C	Britannia C	289	8.01	10204	2576	2.67	1.07
D	Britannia D	109	5.11	14200	4594	2.78	1.37
E	Buchan	106	5.01	21498	6379	4.40	2.06
F	Ivanhoe	194	13.80	25184	4635	5.08	1.86
G	Petronella	63	6.53	56749	12862	6.67	2.47
H	Rob Roy	83	4.81	36893	11986	1.76	0.91
I	Roisin	572	29.34	26686	3292	5.12	1.82
J	Tartan Terrace	360	23.10	21275	4394	4.05	1.66
K	Box 01	76	10.93	13890	3889	4.46	1.86
L	Box 02	860	28.88	20927	3882	7.32	1.81
M	Box 03	25	3.99	69539	18743	6.75	3.17
N	Box 04	386	17.02	177347	5319	17.91	2.08
O	Box 06	84	12.21	15169	3025	6.17	1.58
P	Box 07	138	5.78	46052	11373	5.27	2.49
Q	Box 08	32	6.50	16280	3248	4.50	1.55
R	Box 09	32	2.73	75621	15571	5.99	2.94

SEMI-AUTOMATED CHARACTERISATION OF SEABED POCKMARKS FROM MULTIBEAM BATHYMETRIC DATASETS

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Pockmarks are seabed indicators of focused fluid seepage, most notably gas such as methane, and can occur in vast numbers in many marine and even in lacustrine environments. The presence and distribution of pockmarks need to be considered in the development of any infrastructure at the seabed. However, manual mapping of these features can be extremely time consuming and it is implicitly subjective. For that reason we developed a semi-automated method to recognize, spatially delineate and characterise morphometrically pockmarks at the seabed from multibeam data sets. This type of data set has become a key source of information to study the morphology and distribution of pockmarks at seabed. As modern site investigations regularly include multibeam sonar that collects large volumes of bathymetric data that can be used to produce digital depth models of the seafloor with sufficient resolution to characterize individual pockmarks.

The semi-automated method were presented comprises two scripts, *Pockmark Mapping* and *Pockmark Characterization*, which allow the systematic application of a sequence of well defined tools available within the ESRI ArcGIS toolbox. The input data set required is merely a digital depth model (DDM) that is used to generate three output shapefiles: 1) a polygon shapefile that delineates the pockmarks at seabed, 2) a point shapefile that shows the centroid of the referred polygons, and 3) a point shapefile that marks the deepest point within each pockmark mapped (Figure 1). This last shapefile is likely to correspond to the main source point, or vent, of the fluid escape that originated the pockmark. These output shapefiles include, within their table of attributes, all the morphometric attributes measured for each mapped pockmark: Area (m2), Perimeter (m), Area/Perimeter Ratio, Depth (m), Maximum water depth, Minimum water depth, Maximum Slope, Mean Slope, Azimuth and Major Axis Length.

This method creates the possibility to extract morphologic information of a vast number of pockmarks from multiple surveys in a fast, systematic and consistent way. This is a significant improvement to the study of pockmarks, considering that it would be highly unlikely for one or multiple interpreters to maintain the same criteria throughout the laborious process of manually mapping such number of pockmarks, therefore compromising the possibility of doing any valid statistical comparison between pockmark populations. The application of this method to different pockmark fields, over a wide range of water depths, rheology and grain size of the seabed sediments, composition and nature of the fluid escape, timing, and geological settings, combined with appropriated statistical study of data extracted, could be extremely revealing. Plus, it could also provide a useful data set for quantitative testing of any pockmark formation model.

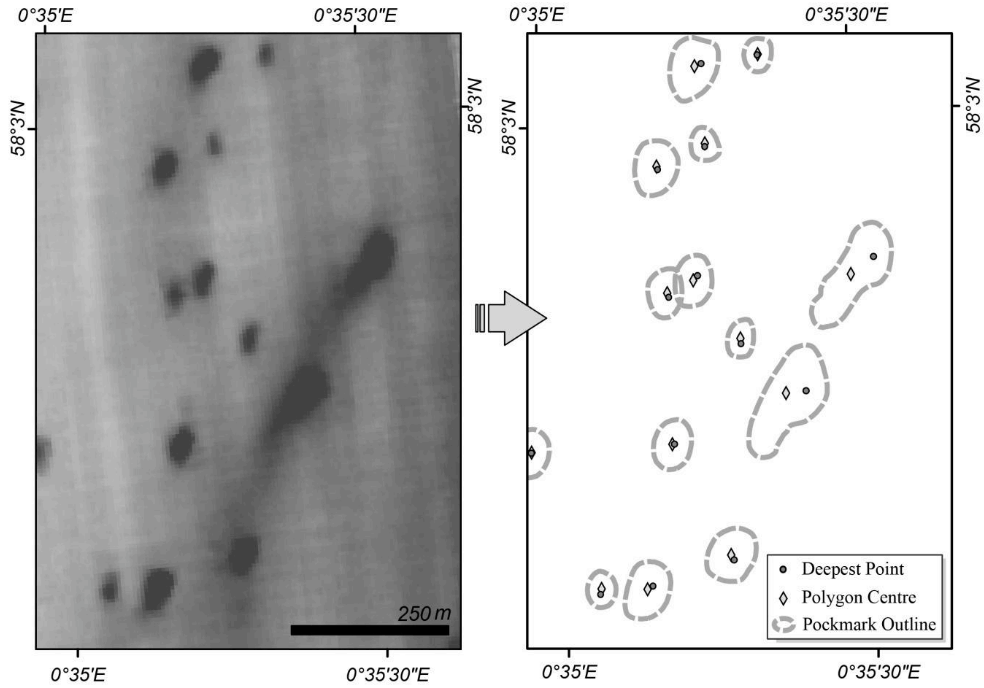

Figure 1- Left: Detail of a bathymetric data set used as input for testing the semi-automated method of mapping and characterisation of pockmarks. Dark grey: deeper water depths, Light grey: shallower water depths. **Right:** The three output shapefiles generated by the method.

SHALLOW GAS AND STRATIGRAPHIC ARCHITECTURE OF THE SEDIMENTARY RECORD FROM AN ENCASED VALLEY: RIA DE VIGO

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The Ría de Vigo, in the northwest Iberian Peninsula, is a large submerged, incised valley which is orientated SW-NE (Fig. 1). San Simón Bay is a small N-S-orientated shallow basin located in the innermost part of the ria and connected to the ria by theRande Strait.

The underlying geology of the Galician coastal area is characterized by granites and by Palaeozoic meta-sedimentary rocks. Major faulting, and orientation of both, ria and bay, suggest that their formation -probably during the Miocene if not more recently- was dictated by the tectonics history.This geological framework, together with the climatic and oceanographic conditions, constitutes the main factors controlling the Holocene stratigraphic evolution and sedimentary facies distributionin the ria.

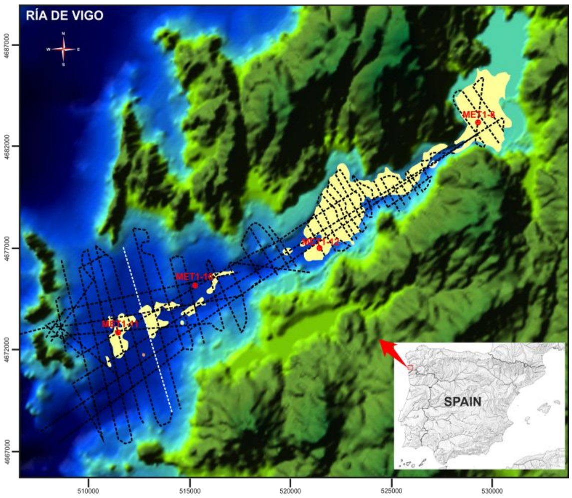

Fig. 1.The Ria de Vigo displaying seismic survey; shallow gas fields and core locations.

The accumulation of Holocene sediment in Ria de Vigo has been studied by the integration of 1) large scale high resolution seismic data, and 2) detailed analysis of gravity cores (textural, geochemical, micropaleontological and radiocarbon dating).

In large areas of Ría de Vigo the seismic records are obscured by acoustic turbidity (Fig.2) which represents gassy sediments. It is possible to distinguish two Quaternary seismic sequences, 1- Upper Pleistocene sequence (SQ1) and 2- Holocene sequence (SQ2). The oldest sequence boundary identified on the seismic records is the erosive and locally discordant surface SB1 (the erosive surface on the Basement, Fig. 2). It is characterised by the presence of channel incisions, which indicate an important relative drop in sea level and the concomitant lowering of the fluvial base level with a migration of facies and coastal onlap towards the main ria basin. This surface represents the erosion due to the drop in the sea level during the Last Glacial Maximum (LGM), 18 ky BP.

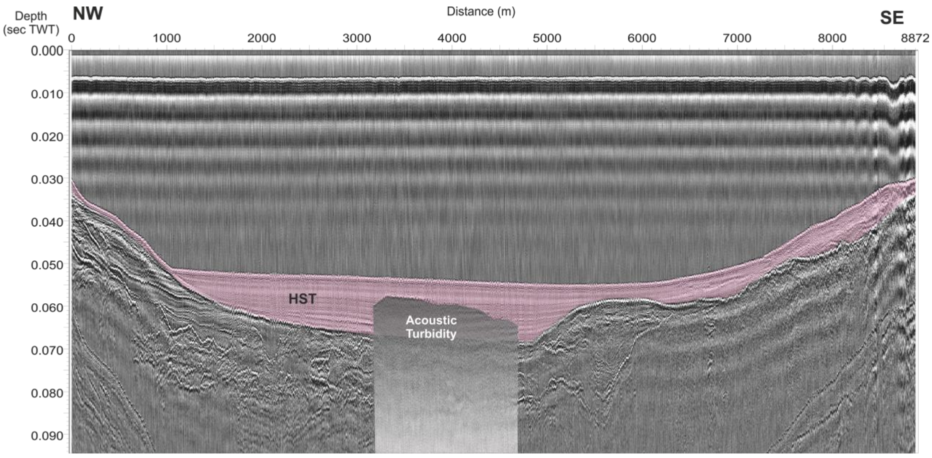

Fig. 2.Seismic line with distribution of HST and acoustic turbidity. See Fig.1 for location.

Seismic sequence-1 (SQ1) sits on the SB1 surface and is composed of two seismic units that represent transgressive pulses (TST) of relative sea level rise during the post-glacial period. The bases of these units are the transgressive surfaces (ts). The top of SQ1 is a new prominent erosive surface (SB2) that correlates withthe Younger Dryas event. This was a time of stabilization/lowering in the relative sea level with sediments prograding into shallow watersof the ria and the incision of channels in the emerged areas. Consequently, SQ1is of Late Pleistocene age and SQ2 represents the Holocene sedimentation.

The Holocene SQ2 is composed by four seismic units separated by minor discontinuity surfaces. These units are progressively more extensive (from bottom to top), showing a clear shifting of the onlap towards the ria basin edges. The three older units of this sequence show a backstepping configuration representing TST pulses in the area. The youngest unit displays basal downlapand progradingclinoforms towards de main ria basin, being attributed to the HST. This youngest unit is affected by acoustic turbidity and other seismic signatures due to the presence of gas within the sediment. Acoustic gas fronts are identified at average depths of 4-5m below present sea bed (b.p.s.b.) in the outer ria and 1-2 m (b.p.s.b). in the inner areas.

The grain size analysis from gravity cores show that this unit is essentially muddy, except in the areas close to the basin edges. Geochemical analysis show high values of TOC (average 3%). Sediment and porewater analyses indicate a distinct sulphate-methane transition zone (SMTZ) ranging from 210-230 cm in the external areas to 60-100 cm in San Simón Bay.

Radiocarbon dating allow to establish seal of gassy sediment is 3800 cal.yr BP in the external riawhile in San Simón Bay gassy sediments are as young as 450 cal. yr BP.

Acknowledgements:
This work was funded by the Ministerio de Ciencia e Innovación (MICINN) under research projects CTM2009–13926-C02-01 and CTM2009-08158-E, and by Xunta de Galicia project 10MDS310020PR. N. Martínez-Carreño was funded by the FPI research Grant from MICINN. We would like to thank Seismic Micro-Technology Inc., who provided free Licences of Kingdom Suite software.

COLONIZATION OF ARTIFICIAL SUBSTRATES (CHEMECOLIS) IN DEEP-SEA EUROPEAN REDUCING HABITATS BIODIVERSITY, SYMBIOSIS AND GEOLOGICAL FACTORS

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The discoveries of new types of ecosystems on mid-ocean ridges and continental margins have changed our vision of biodiversity into the deep sea. The energy supply to these communities rely on methane- and sulphide-oxidizing microbes which are unique in their ability to satisfy their carbon and nitrogen needs from inorganic sources, under free-living forms or symbiotic association with invertebrates. Geologically-driven sources of such reduced compounds to the deep-seafloor (hydrothermal vents, methane seeps) are mostly ephemeral and discretely distributed, such are massive organic inputs (whale carcasses, sunken woods) that harbour species closely related to vent and seeps endemic taxa. These fragmented reducing habitats, however, markedly differ in their chemical/biogeochemical features and temporal dynamics. Since 2006, standard colonization device named **CHEMECOLI**s (**CHEM**osynthetic **E**cosystem **CO**lonization by **L**arval **I**nvertebrates), filled either with organic (wood and alfalfa) or mineral substrates (carbonates) were deployed in different deep-sea reducing habitats for different period of time (2 weeks, 1 year, 2 years and 3 years) in order to reproduce and understand the establishment of reducing habitats: 1) MoMAR hydrothermal sites on the Mid-Atlantic Ridge (Rainbow and Lucky Strike), 2) Haakon Mosby mud volcano (HMMV) in the Norwegian sea, 3) Nile deep-sea fan brines and seeps areas in the eastern Mediterranean. Here we will present results on metazoan species richness that colonized as larvae CHEMECOLIs, highlighting those that are chemosymbiotic species, opportunistics and tolerant to sulphide. Data from these experiments contribute to the understanding of deep-sea species dispersal potential between patchy and ephemeral deep-sea habitats. Some data may show as well evidenced of methane derived authigenic carbonates.

Submarine investigations of the submerged section of the North Anatolian Fault within the Sea of Marmara opens new perspectives for the deep seafloor monitoring of earthquake hazards

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The Istanbul region, located near the submerged North Anatolian Fault (NAF) in the Sea of Marmara (SoM), is one of the most adapted areas to test models aiming at improving the predictability of earthquakes because : i) there is a high probability that an earthquake of Mw > 7.0 will strike within the next decades along the NAF in the Sea of Marmara, directly affecting the heavily populated Istanbul area; ii) the segment having the highest probability to rupture is relatively well determined ; iii) Recent work has reported tremors at least 44 minutes before the Mw 7.4 Izmit earthquake, which devastated part of north western Turkey in 1999 *[Bouchon et al, 2011] ; iv)* Gas emissions were found in the water column near the surface expression of known active faults *[Géli et al, 2008]*. Here, we present high-resolution, 3D seismic data, heat flow data and geochemical data collected in 2009 during the Marmara-Demonstration Mission of the ESONET Programme (European Seafloor Observatory Network. The data, collected from where the NAF cuts a gas reservoir from the Thrace Basin province, show a diapiric feature that pierces the seafloor, within less than 1 km of the fault zone. It is proposed that at greater depth, the fault must interact with the source of the gas. This hypothesis could open new perspectives that were not even imaginable a few years ago, and supports the necessity to monitor gas emission activity along with seismicity. If seismic tremors or other anomalous seismic activity are found to be associated with anomalies in gas emission activity, then we will have more criteria for identifying that an anomalous and potentially dangerous situation is under way.

A case study of fluid venting structures and amplitude anomalies as indicators hydrocarbon leakage in interplay with geological setting, Neogene-Quaternary interval of Lower Congo basin

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Localized fluid venting structures in the Neogene-Quarternary interval of Offshore Congo Basin, have been noticed to be associated with particular types of geology features in a high resolution 3-D seismic survey.

Venting structures represent various regimes of methane seepage after literature (cf. Hovland & Judd, 1987, Robert, 2001, Gay, 2002, Cartwright et al., 2007). Their stratigraphic positions indicate timing of leakage, and their relative chronologies in vertical successions imply fluid fluxes varied overtime. The distributions of venting structures in this survey indicated that leakage pathways are susceptible of being controlled by the development of various types of geological features. The fluid venting structures that we focus on are preferentially concentrated at location where associate with special geologic setting (Fig. 1). These associations are the following:

(1) Seismic chimneys associated with positive or negative high amplitude anomalies (HAAs) located within two mass transport complexes (MTC) which were adjacent to the diapir flanks: i) the very localized linear HAAs that occur at the MTC base, evolve upward into a trail of stacked-up circular positive HAAs, which are conditioned by a polygonal fault cell in the interval above (Fig. 1a). ii) Sub-circular positive HAAs succession occurred at a MTC centre. The MTC is affected by the isotopic polygonal fault network and shows negative HAAs at its surface (Fig. 1b).

(2) Advancing pockmark trails were observed to occur above pale-channel complexes and above salt-related fault sets (Fig. 1c).

(3) Small elongate pockmarks, from tens to a hundred meters occurred above salt-withdrawal syncline (Fig. 1d).

(4) Vertically stacked pockmarks (over a hundred meters) are associated with seismic chimneys occurred on the foot-wall of major growth fault (Fig. 1; 3D dip horizon of 5.3 Ma).

(5) Linear conduits associated with PHAAs occur along the polygonal fault networks, are located round the salt-redraw syncline next to the diapir (Fig. 1e).

These geological features exerted influences on the degree of contemporary leakage in different locations of the basin, and thus took control on the evolution of venting structures over time.

We investigated amplitudes and geometries variations in geometry and seismic amplitude of these venting structures, taking into consideration the associated geological features, in order to understand how fluid migration is affected by tectonic evolution and morphologic setting on the continental slope.

At the early stage of the study we present here first, the seismic character of these venting structures that we are using to reconstruct the fluid migration history in this part of basin.

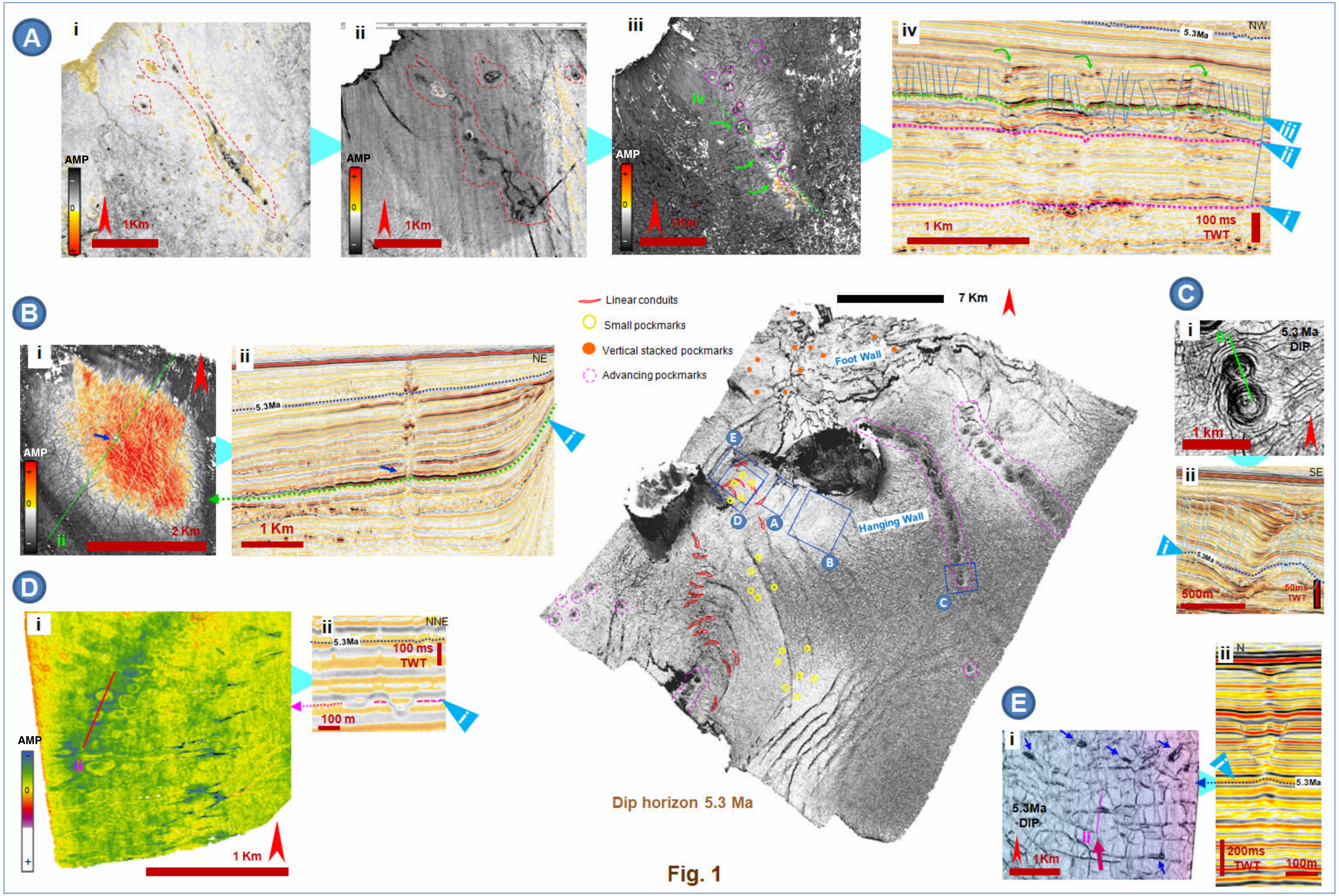

Figure 1: Distributions of fluid venting structures in the study area, are showed on the 3D dip horizon (5.3 Ma). Locations of different types of venting structures are indicating by the corresponding letters on the 3D dip horizon.

MECHANISM OF GAS EMISSIONS OFF SW TAIWAN

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Methane escape from the seafloor is a widespread phenomenon and its consequences impact not only on the geosphere but also on the biosphere, the hydrosphere and the atmosphere. Through gas seepage, the over-pressure pore-fluid in gassy marine sediments migrates upwards and creates pockmarks and mud volcanoes as it emerges from the seafloor. Like most of the continental margins, mud volcanoes and methane emissions are distributed in the convergent margin off SW Taiwan. Here, we show that the mechanism and intensities of methane emissions from the seabed off SW Taiwan strongly depend on the ocean tides of main lunar semi-diurnal and diurnal constituents with periods of 12.4 and 25.6 hours, respectively. The gas expulsions have induced tremors. The tremors have created low-frequency harmonic oscillation of the seafloor;the persistent oscillation of the seabed may enhance seafloor instability and cause potential for submarine landslides.

GAS IN MARINE SEDIMENTS: WHAT MAKES IT DIFFERENT?

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Seismic-scale sediment remobilization by fluid circulation is increasingly recognized as a pervasive phenomenon in sedimentary basins. All fluids can lead to remobilization, provided the stress exerted by their flow exceeds some resistance of the sediment they flow through. Depending on the rheology of the material, this interaction can take many different forms.

The issue addressed here is that of the specificity of methane gas with respect to other common subsurface fluids, primarily water. Although water is considered here as one fluid, variations in salinity / mineral content actually make it a full spectrum, from fresh meteoric water to saturated brines, with a wide range of pH resulting in different modes of interaction with sediment. Liquid hydrocarbons make another fluid spectrum, often associated with gas. Gases of course include methane, but also CO_2, H_2S, hydrocarbon gases with higher C number, etc.

The following characteristics of methane are thought to give it a specific role in sediment remobilization, and can help discriminating the past migration of gas from water flow:

- Gas in general, methane in particular, is buoyant, and has a natural tendency to move up the stratigraphy as much as it can. What is worse, free gas expands while doing so, creating a positive feedback loop; the very loop that can result in well blowouts, by the way. And on a gentler note, in pockmarks of various shapes and sizes.

- Methane is soluble in water (a few g/l under typical geopressures in deep water, say 100 to 300 bar) and much more so in oil, and typically with a positive pressure dependence. This means that water with enough dissolved methane may exsolve it inside the sediment, likely provoking mechanical modifications such as liquefaction (cf. the “soupy” or “moussy” texture often observed in gassy sediments).

- Many gases, methane in particular, combine with the omnipresent water of sedimentary basins to form solid clathrates under suitable (P, T) conditions that are normally met below the seafloor in deep water. The process is reversible, but a cycle of hydrate formation followed by dissociation or dissolution is very unlikely to leave the sediment unaffected during the process. Many disturbed sediment packages conveniently interpreted as debris flow beds may turn out to be hydrated (in the sense of hydrate-bearing), then de-hydrated sediments once we figure out what the result is precisely meant to look like.

- Finally, in the methane-sulfate transition zone (typically a few meters to tens of meters below the seafloor), methane and sulfate are used as an energy source by bacterial consortia (Boetius et al., 2000). One by-product of very special interest to seismic interpreters is high-impedance carbonate, which often contrasts with background sediments so as to make bright patches that fossilize past gas migration in a seismically visible way.

Several uncertainties remain, especially regarding more quantitative parameters. However, it is thought that examining seismic evidence of sediment remobilization through the filter of the four points above will help assessing the nature of the fluid that caused it, especially discriminating between gas and other fluids.

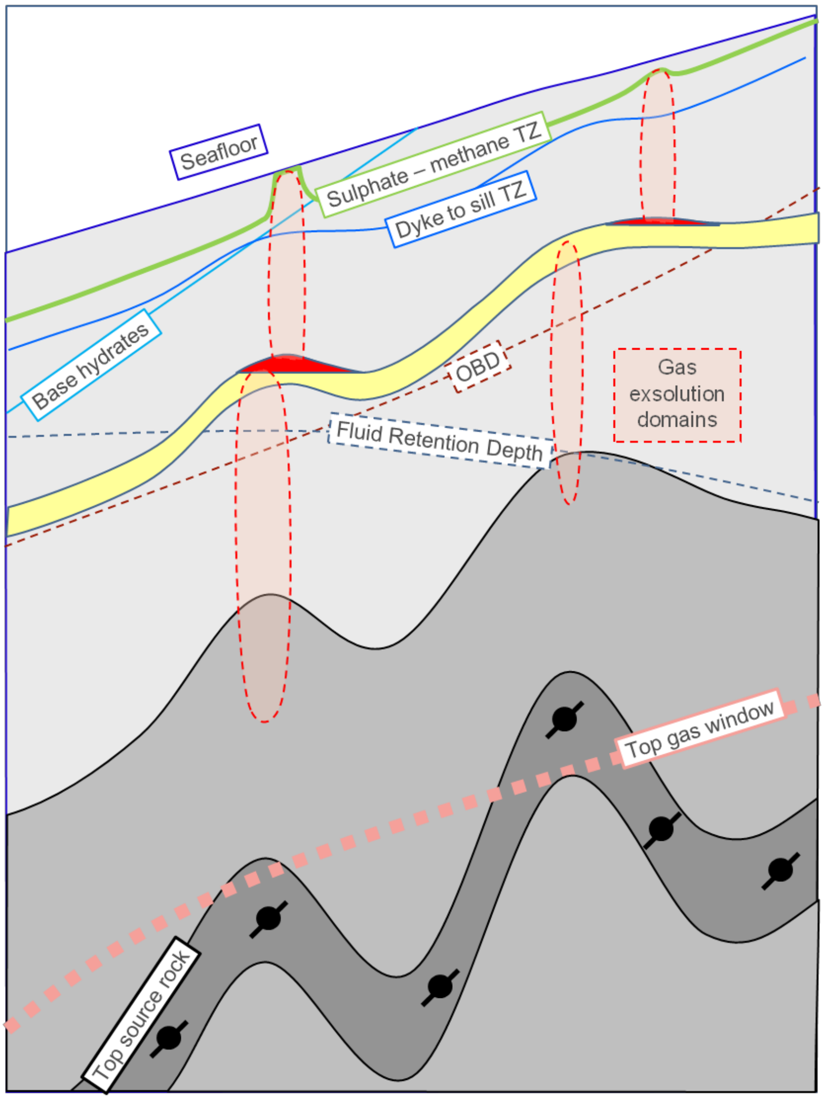

Fig. 1: Domains that are relevant to the analysis of fluid remobilization in subsurface. Some of them are related to the migrating fluids (e.g. base of the hydrate stability zone or OBD, base of oil biodegradation, a powerful gas-making process) while others are more related to the properties of the host sediment (e.g. the fluid retention depth (Swarbrick et al., 2002))

SUBSURFACE FLUID-FLOW PATTERNS WITHIN THE GAS-HYDRATE STABILITY ZONE OF THE BLACK SEA

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Methane seeps are a widespread phenomenon in the Black Sea and those seeps showing the presence of gas bubbles while being located within the zone of gas hydrate stability are of particular interest. Different scenarios have been proposed in order to explain the presence of free gas. They include localized elevated heat flow in conjunction with mud extrusion, excess gas so that not enough fresh pore water is available to form gas hydrates, methane flux out of contact with the surrounding pore fluid and the presence of higher hydrocarbons resulting in the formation of structure II hydrates. All these scenarios, however, do not consider timing as an important criterion. How pervasive is the distribution of gas hydrates within its stability zone? Does the formation of seeps predate or postdate the establishment of the gas hydrates or is it concurrent? These are some of the remaining open questions regarding cold seeps in deep water.

Some possible answers might be given by looking at the three-dimensional subsurface structure of the Kerch Flare, which is located in roughly 1000 m water depth south of Kerch Strait in the northern Black Sea. The shallow subsurface structure of this cold seeps site has been recently imaged using 3D-seismic data indicating that Kerch Flare formed on the levees or intercanyon deposits of the Don-Kuban Fan that are up to 200 metres in thickness. The seep is located at the top of a ridge (levee) like many other cold seeps worldwide. However, the seep location does not coincide with anticlinal structures in the subsurface. The seep site developed along subvertical normal faults and can be traced down below the base of the levee deposits. The actual source of the seep has not been imaged but we speculate that regional tectonic structures determine the presence of the seep and the fluid pathways from depth to seafloor. The faults are postdepositional and the presence of gas hydrates might have aided fracturing of the well-stratified levee deposits by favouring brittle behaviour. In addition, the presence of gas hydrates would have prevented rising gas from being in contact with pore fluid so that additional gas hydrates could not form. In this respect Kerch Flare constitutes a good example for one of the possible scenarios in order to explain the presence of free gas within the gas hydrate stability zone. A deep fluid source and fractured pathways differs from other cold seeps in the deep Black Sea like Pechori and Iberia mounds offshore Georgia and the mud volcanoes of the Black Sea that are both associated with diapirism at depth. It is also unlike Batumi seep offshore Georgia. Here, the gas is biogenic and its source is shallow. Coexistence of gas and gas hydrates in this case is likely the result of excess gas with respect to fresh pore water.

The subsurface structure of cold seeps appears to be even more complex that we thought and more high-resolution 3D-seismic studies are needed in order to better understand these structures.

Distribution of light hydrocarbons in marine sediments (results of regional studies, South Russia)

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Regional studies on distribution of light hydrocarbons (HC) in marine bottom sediments (Sea of Azov and Black Sea) have been shown, that migration from the deep part of sediment cover up to the surface (sea bottom) is the main factor, which determines the hydrocarbons (C_1-C_6) spatial distribution in the marine sediments, and contribution of biogenic and anthropogenic factors is insignificant. It is also have been shown, that background levels of light HC depend on the geological structure of the basin and vary in different structural zones. (Lavrenova et. all 2006, 2010, Kruglyakova et. all, 2010)

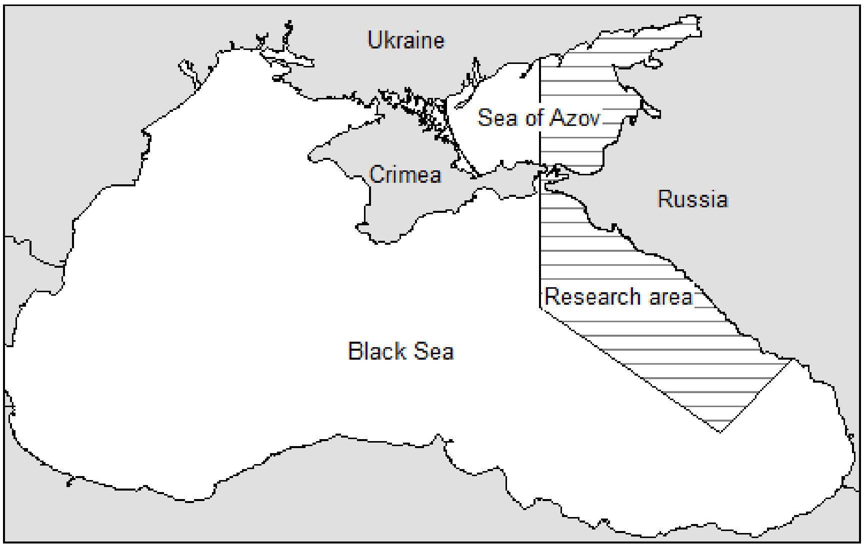

Figure 1 *General chart of geographical position*

Sea of Azov and the Black Sea are well-known oil and gas bearing basins. So, for better interpretation gas-geochemical data, results of numerical basin modeling and petroleum system modeling (Lavrenova&Kruglyakova 2010, Lavrenova et. all 2011) were examined. Results of united interpretation of geochemical and modeling data are submitted in this paper.

Dependence between spatial light HC distribution in the bottom sediments and specific features of investigated petroleum systems was ascertained.

In particular it is proved:

- presence, age and amount of petroleum systems in the sediment cover cause the background levels of light HC in bottom deposits and its (light HC) composition.

- large-area anomalies of light HC in the bottom deposits locate above the pods of source rock (petroleum system kitchen).

- small-area anomalies in the bottom deposits locate above petroleum accumulations in the sediment cover.

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DEEP SEEP BUBBLES REACH FOR THE SKIES: GROWING EVIDENCE OF BUBBLE-MEDIATED METHANE HYDROCARBON TRANSFER FROM DEEP WITHIN THE HYDRATE STABILITY FIELD TO THE ATMOSPHERE

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Studies of seep bubbles in shallow water (20-70 m) show that a wide size-range of single bubbles can transport a significant fraction of their seabed methane content to the sea surface. Similar conclusions were reached for bubble plumes associated with gas hydrates at Bush Hill (GC185) in the Gulf of Mexico from 550-m water depth if the bubbles were oily; however, subsequent consideration of pressure effects showed that large, non-oily bubbles from such depths could reach the sea surface. Studies for a blowout in shallow water (20 m) and of plume processes (20-70 m) suggested plume synergies can amplify vertical transport, increasing bubble survival. Telltale signatures of plume processes were found for Bush Hill, demonstrating these synergies across half a kilometer of water column. Meanwhile investigation of Structure I gas hydrate bubble skin effects suggested bubbles from deep within the Gas Hydrate Stability Field (GHSF) could reach above the top of the GHSF, consistent with published sonar observations of bubbles rising several kilometers in the GHSF.

More recent data from the Gulf of Mexico, Hydrate Observatory (MC118) from 980-m water depth shows that plume processes can occur across a kilometer of water, transporting methane and other thermogenic hydrocarbons from well within the GHSF to the winter mixed layer (WML) and directly to the atmosphere. Structure II gas hydrate processes were identified as important. Meanwhile sonar data of bubble plumes from Hydrate Ridge, offshore Oregon in 800 m water show similar plume survival across most of the water column; even though higher hydrocarbons than methane are absent. Numerical bubble model results show that large bubbles can reach the WML from these depths. Meanwhile the limited available data for the Deepwater Horizon (DWH) suggests methane did not reach the atmosphere from 1.5 km. The unique character of the DWH plume compared to typical marine seepage suggests it is a poor model for understanding natural processes. Other studies suggest currents and a well-defined thermocline are critical factors, although subsea dispersants, possible gas hydrate dissociation, and a paucity of data caution against drawing wide-ranging conclusions from this anthropogenic event.

SULFUR ISOTOPIC VARIATION AND ROLE OF SULFATE IN THE FRESHWATER METHANE-RICH LAKE BAIKAL : CARBON/SULFUR CYCLING

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Lake Baikal is the world deepest and one of the largest freshwater lake with limited sulfate supply entering the lake at present time. While sulfate is an important oxidant in the organic carbon cycling in seawater environment, convincing evidences showed that sulfate supply may have varied in the past geological time and may alter carbon cycling in the Lake. The objectives of this study are to identify sources of sulfate in the lake region, C/S records in lake sediments in order to evaluate the role of sulfate in the methane rich freshwater environment.

We have collected lake waters, river waters, spring waters in the region, and cores in the lake. Dissolved and pore water sulfate, chloride, sediment organic carbon, nitrogen, pyrite and sulfur isotopic value of sulfate and pyrite were analyzed. Large variations existed in waters in the surrounding areas near the lake. Water in the Lake Baikal is well mixed with sulfate concentration at 64.2 ±0.5µM, chloride 21.4 ±1.1µM and sulfate-S isotopic value at 7.7±0.3‰. The surrounding rivers show large variations with some reaching 800µM (sulfate) with sulfate sulfur isotopic values varying between +20.8 to -6.9‰. Spring water sulfate S could reach $\delta^{34}S$ values as high as +29.3‰ with sulfate concentration up to 4300 µM. These variations demonstrate that river may not be the only source of sulfate in the lake whereas spring waters from hydrothermal process may have been another source in the geological history. Unusual peaks of pore water sulfate, approximately 80 times higher, were found in sediments, which also indicate that other source of sulfate exists in this lake environment. As a result of AOM, extra source of sulfate provides additional pyrite formation as evidenced from the extremely high pyrite concentrations in sediments. Contrary to areas without AOM, little extra pyrite formation was found.

Acknowledgement: This project is supported by Taiwan NSC (NSC100WFA0101048 and 99-2923-M-002-005-MY3) to SL and Russian Foundation for Basic Research(# 10-05-92004-NNS) to GVK.

STUDY ON DIVERSITY OF BACTERIA PARTICIPATING IN CYCLES OF METHANE AND AMMONIUM AT SITES OF HYDROCARBON DISCHARGE IN LAKE BAIKAL

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Recent studies of freshwater ecosystems have shown that specific bacterial group of the phylum *Planctomycetes* and bacterial group anammox participate in anaerobic methane oxidation (Van de Graaf et al., 1995; Kuypers et al., 2003; Ettwing et al., 2010). Representatives of the phylum *Planctomycetes* also participate in nitrogen cycle, including anaerobic ammonium oxidation (ANAMMOX), in freshwater and marine ecosystems (Mulder et al., 1995; Van de Graaf et al., 1995; Kuypers et al., 2003). Anaerobic methane and ammonium oxidizing bacteria can coexist utilizing nitrite as electron acceptor for oxidation of methane and ammonium (Zhu et al., 2010).

Natural hydrocarbon discharges have been identified in Lake Baikal using different methods; mud volcanoes, methane seeps, near-surface occurrences of gas-hydrates (GH) (De Batist et al., 2002; Klerkx et al., 2003; Khlystov 2006; Granin et al., 2010) and natural oil discharges (Khlystov et al., 2007; Kontorovich et al., 2007) have been found in different parts of the South and Central Baikal. These sites, in comparison with the test ones, have shown high concentrations of ammonium (up to 40 mg/L), bicarbonate ions (up to 183 mg/L), and total Fe (4.7 mg/L) in surface sediments. We have studied microbial diversity in surface and deep-water sediments of cold seeps with different hydrocarbon structure using universal Eubacteria-specific primers and specific primers for *Planctomycetes*, anammox, and methanotrophs (pmoA gene). Comparative analysis of nucleotide sequences of 16S rRNA gene fragments from the site of natural oil discharge, Gorevoi Utes, has indicated different microbial composition in the studied samples. The most diverse microbial community was obtained from surface sediments, where we have identified representatives of the phyla *Bacteroidetes, Proteobacteria* (β, γ, and δ), *Verrucomicrobia*, *Nitrospirae*, *Chloroflexi*, *Planctomycetes*, *Acidobacteria*, *Chlorobi*, and *Actinobacteria*. In reduced sediments, there was less diverse microbial composition represented by the phyla *Bacteroidetes, Firmicutes, Actinobacteria,* and *Proteobacteria* (α, β, and γ).

Using *Planctomycetes*-specific primers, we have obtained the positive result only for DNA from surface layer of bottom sediments where high ammonium concentrations were observed. Analysis of *Planctomycetes* from the clone library has shown a significant diversity of its representatives in the studied community. We have found representatives of the species *Planctomyces*, *Pirellula*, *Gemmata*, *Isosphaera* which inhibit such freshwater and marine ecosystems as Lake Tanganyika (Schubert et al., 2006), the Elbe River, and the Baltic Sea. Among representatives of the species *Pirellula*, we have detected nucleotide sequences 92% similar to bacteria participatinig in anaerobic ammonium oxidation. One phylotype belonged to the cluster of ammonium oxidizing candidate species (ANAMMOX group) with 94% similarity (Schmid et al., 2005). *Planctomycetes*-specific primers allowed us to identify *Acidobacteria* and *Verrucomicrobia* (p. *Lentisphaera*) representatives which closest relatives had been isolated from the freshwater Lake Washington and the Gulf of Mexico, and from hydrocarbon-contaminated soils. In addition, representatives of the phylum *Verrucomicrobia* are known to participate in methane oxidation (Pol et al., 2007), and we have also detected them by pyrosequencing in surface and deep-water sediments near Cape Gorevoi Utes. Fluorescence in situ hybridization (FISH) with labeled oligonucleotide probes for the phylum *Planctomycetes* has indicated its representatives in microbial community near the cold seep site Bolshoe Goloustnoe.

Using *pmoA*-gene specific primers has allowed us to detect sequences participating in anaerobic methane oxidation in surface layer of bottom sediments near Cape Gorevoi Utes, where representatives of type I methanotrophs dominated.

Therefore, at the sites with cold seeps in Lake Baikal we have detected various phyla of bacteria participating in methane oxidation (methanotrophs), and bacteria of the phyla *Planctomycetes* and ANAMMOX group which utilize nitrite resulted from ammonium oxidation as electron acceptor.

This work supported by the Presidium of the Russian Academy of Sciences, Program 23 (Project 23.8), the RFBR Grant No. 10-05-00681, and Integration Project No. 82.

METHANE DYNAMICS IN SEVASTOPOL BAY (BLACK SEA)

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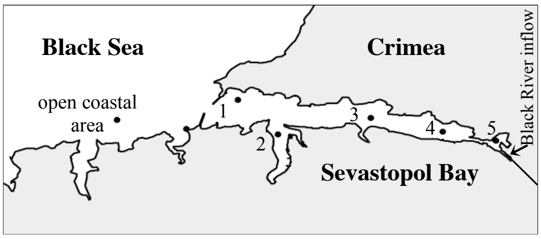
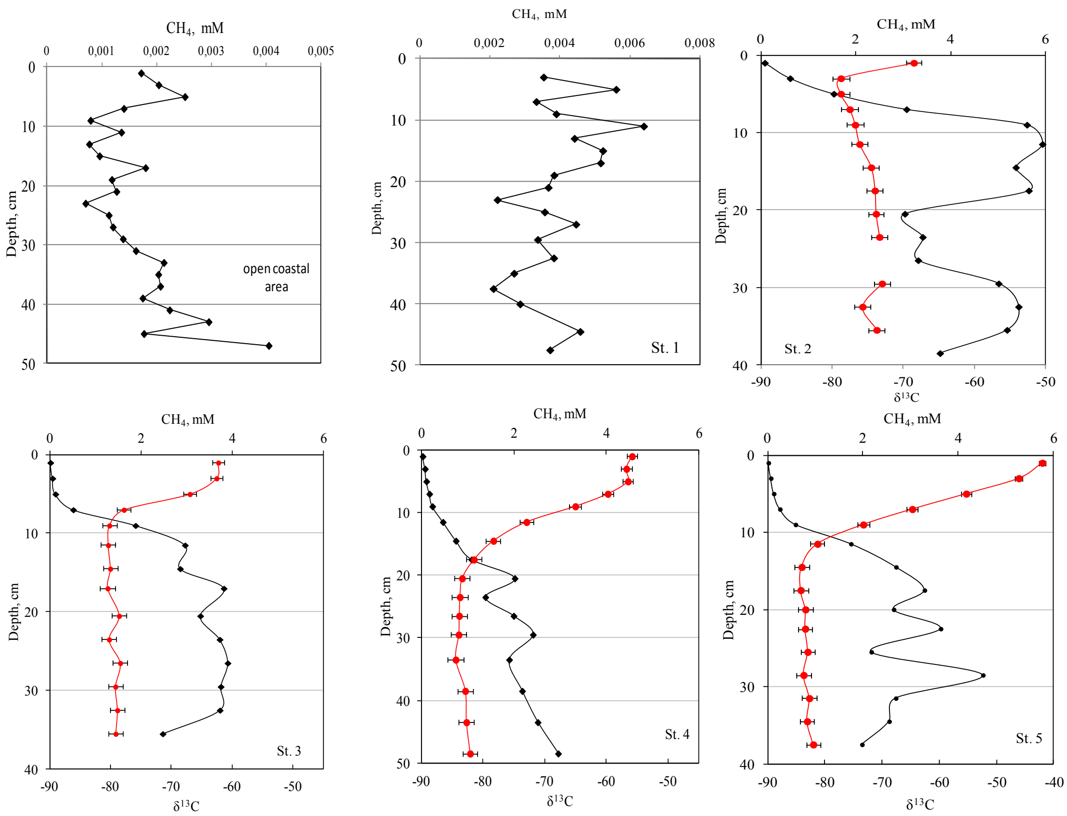
Sevastopol Bay, located along the SW Ukraine Black Sea coast, is a semi-enclosed estuarial bay which length is about 7 km and maximal depth is 20 m. During the last years number of shallow gas seepages have been found here.

Methane concentration, exchanges at the sediment-water interface and emissions to the atmosphere were studied along the Sevastopol Bay as well as stable carbon isotopic ratios of CH_4 dissolved in sediment pore water in order to evaluate its origin and fate during upward migration towards the seafloor. The methane concentration in the upper layers (50 cm) of bottom sediments in the inner part of the Sevastopol bay reached 5.9 mM, which is three orders of magnitude higher than values in the same layers of open coastal areas of Sevastopol (Fig. 1).

Fig. 1. Schematic map of the Sevastopol Bay area indicating sampling positions and depth profiles for CH_4 concentration and $\delta^{13}C$. Note: there is no $\delta^{13}C$ data for St. 1 and profile from adjacent coastal area because of methane concentrations which were too low for isotopic analysis.





It was found, that the maximal CH_4 concentrations in central and apex parts of the Bay exceeded its solubility in the pore water, testifying to the presence of gaseous methane together with dissolved one at this study sites. The point of methane oversaturation is reached at 10-15 cm depth bsf. The positive correlation between methane and organic carbon concentration levels in the sediments profiles was revealed, with a correlation coefficient (R^2) of 0.9.
In the uppermost sediments, methane is significantly reduced either due to diffusion into methane-depleted bottom waters or due to the sulfate-dependent anaerobic oxidation of methane. The vertical trends in $\delta^{13}C$-CH4 values show that methane is considerably depleted in ^{12}C in the uppermost sediments. Therefore, the low methane concentrations in top sediments predominantly result from microbial methane consumption. The methane hydrocarbon isotope composition at the depth of about 10 cm bsf varied from -85 to -75‰ testify to its biogenic nature.
The methane diffusion fluxes determined by a Fick's first law were directed from the bottom sediments into the water column in contrast to the deep-water Black Sea part. The fluxes did not exceed 1.5 $\mu mol \cdot m^{-2} day^{-1}$ for the open areas and changed from 10 to 544 $\mu mol \cdot m^{-2} day^{-1}$ for the inner part of the bay (Fig. 2). By extrapolating values obtained in 2007-2008, CH_4 emission from the Sevastopol Bay water surface to the atmosphere was estimated to be $2.9 \cdot 10^3$ $mol \cdot day^{-1}$. The contribution from the shallow area of 0 – 5 m depth 1.5 times exceeded the flux from the other deeper part of the bay. The resident time of the dissolved methane in the Sevastopol bay relative to water-air emission as a methane sink ranged from 9 hours to 1.5 days.

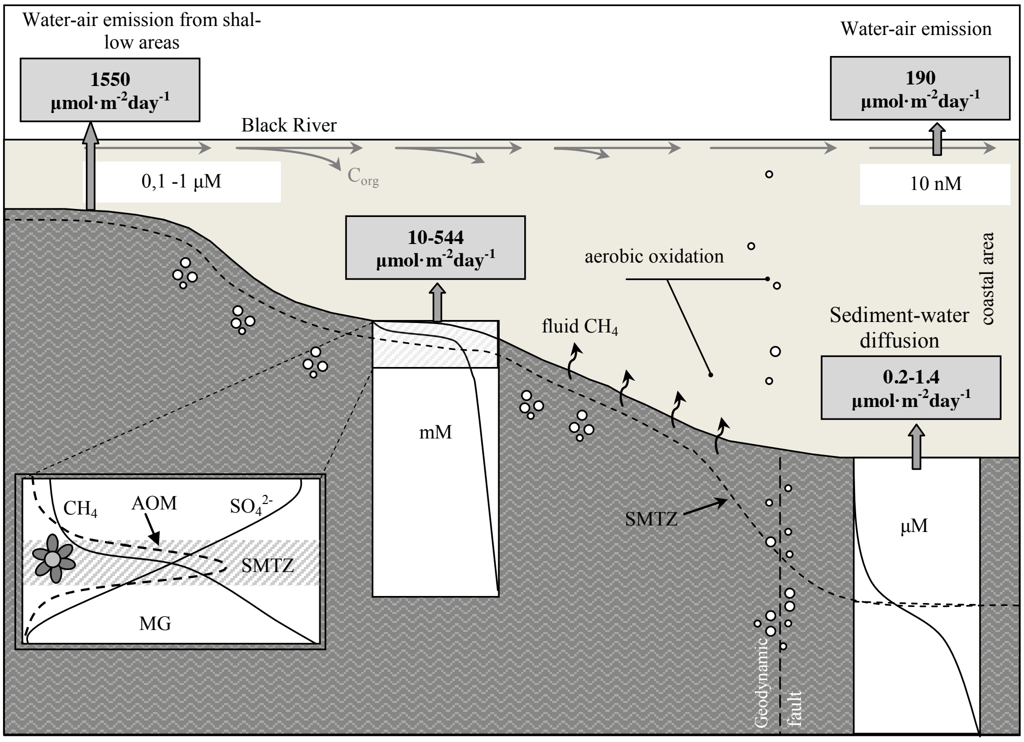


Fig. 2. Schematic overview of major components of CH_4 balance in the Sevastopol Bay and adjacent coastal area: level of sediment and water concentrations, sediment-water diffusion and water-air emission fluxes. Scheme shows the geodynamic fault (vertical broken line) which is confined to the gas seep site.

This work was supported by the MARUM during the Summer Student Fellowship 2011.

MUD VOLCANOES AND FLUID SEEPAGE IN THE MEDITERRANEAN DOMAIN

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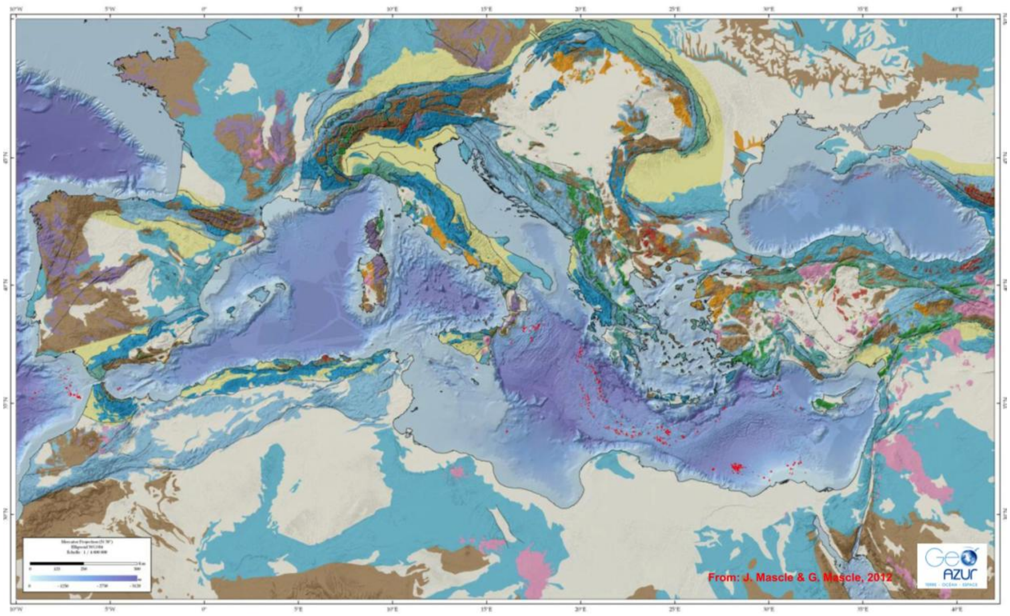
In order to compile, under Arcgis environment, a geological and morpho-tectonic synthesis of the Mediterranean domain (Mascle & Mascle, 2012) we have selected a series of geological parameters of the Mediterranean Sea, which we consider as characteristic of the area. Among them, the repartition of massive mud/fluid expulsion on the sea floor, commonly known as mud volcanoes and/or gas chimneys.



Distribution of the main identified mud volcanoes and gas chimneys in the Mediterranean domain and surroundings (Gulf of Cadiz and Black Sea). The fluid-related features (red dots) are shown on a morpho-bathymetric synthesis of the Mediterranean Sea recently published (Brosolo, Mascle & Loubrieu, 2012). The onshore, simplified, geological synthesis is extracted from Mascle & Mascle (2012).

In the Mediterranean Sea these features, selected either on the basis their identification by sampling, direct in situ studies and/or specific morphology and backscatter signatures are not randomly distributed. Their distribution is first controlled by: - the overall geodynamic framework: mud volcanoes are chiefly documented on thick and over pressured tectono-sedimentary wedges such as the Mediterranean Ridge, the Cyprus arc, the External Calabria arc and within the Gulf of Cadiz accretionary wedge. Massive mud/fluid expulsion features, not necessarily associated to brines, can however been observed along some passive margin segments, for example on the upper slope and at the north-western foot of the Nile cone; some mud volcanoes have also been described in active extensional setting such as in the Western most Alboran Sea and locally along the South-western margin of the Tyrrhenian Sea.

- A second important parameter controlling the occurrence of fluid seepage on the sea bed clearly relate to the presence, or not, of thick Messinian evaporite; in the deep Mediterranean basins, when the upper sedimentary cover includes massive Messinian salt (as inferred from its seismic facies and velocities), fluid seepage features can hardly been documented; this is likely due to an efficient cap-rock play of the Messinian strata through which fluids cannot be expelled unless existing fractures.
- The third controlling factor on mud volcanoes repartition in the Mediterranean Sea precisely relates to the occurrence, or not, of tectonics. These can be active thrusts and associated fractures, for example along the contact of the Mediterranean Ridge with its backstop, or growth fault systems generated by salt-driven gravity tectonic and rupturing thick Messinian salt layers such as at the foot of the Egyptian continental slope.

FREE GASES IN GAS HYDRATE MOUNDS AS MEASURED BY TDR, JOETSU BASIN, EASTERN MARGIN OF JAPAN SEA

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Massive gas hydrates are exposed atop the partly collapsed gas hydrate mounds, 30-50 meter high and 300 to 700 m in diameter, on spur and knoll in the Joetsu Basin, 900 to 1000m W.D., eastern margin of Japan Sea, in close relation with methane seeps, bacterial mats, and methane-induced carbonates. Gas hydrates are composed dominantly of thermogenic gases with $\delta^{13}C$ of -30 to -50‰, while gases in sediments are predominated by microbial (-45 to -101‰). Headspace gas analysis of deep cores (~2000mbsf) has revealed a rapid upward shift ingas composition (C1/C2+C3) and $\delta^{13}C$ of methane at around 1200 mbsf from thermogenic to microbial, however, gases in gas chimneys are still enriched in thermogenic even in shallow sediments. Joetsu gas hydrate fieldis characterized by low bottom water temperature, 0.3°C, and high heat flow, 90-100 mK/m. Then the depth of BSR is estimate to be 115 to 130 mbsf, while the TWT depth of BSR is observed at 200 to 210 ms, which implies that the Vp of gas hydrate bearing sediments on the mounds above gas chimneys are 1100 to 1300 m/sec, extremely low as hemipelagic mud. This anomaly suggests an existence of significant amount free gas in gas hydrate stability zone of gas chimneys. Active and widely distributed gas seeps on and around gas hydrate mounds also indicates existence of free gas bubbles within shallow subsurface zone of gas hydrate mounds. Water and gas contents of deep sediments of gas hydrate field are critical factor to understand the stability of gas hydrate, but it is not easy to obtain precise values on cored sections after core recovery. We conducted *in situ*measurements of the water and gas contents by means of TDR (Time Domain Reflectometry) method. The TDR sensors were installed at the bottom of gravity corers, slowly penetrated into gassy sediments, and the experiment has revealed high gas content in gas hydrate bearing sediments. Preliminary results of our experiments imply that the shallow gas hydrates are closely associated with free gas bubbles, then, the acoustic characterization may mislead us to underestimate the amount of gas hydrate.*Acknowledgements:* Composition of head space gases were taken from the report of JNOC(JOGMEC)/JAPEX in 2004.

CONSTRAINING THE METHANE CYCLE THROUGH CARBON ISOTOPE MODELS

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The amount and formation rate of methane in marine sediments is a crucial aspect when determining both the methane fluxes towards the ocean-atmosphere system and the potential for dissolved methane to form other phases (e.g. free gas and hydrate). Nevertheless, due to the low methane solubility at ambient pressure (ca. 1.5 mM for average seawater temperature and salinity) methane degassing upon core retrieval limits the accuracy of methane concentrations measured above 1.5 mM. While several tools have been developed that may tackle this problem (e.g. autoclave coring), these methods may not be readily available nor practical for the entire scientific community. Nevertheless, diagenetic models which simulate both δ^{13}C-methane and δ^{13}C-DIC (dissolved inorganic carbon) can not only be used to better infer methane concentration profiles, but may also provide a comprehensive method for constraining methanogenic and methanotrophic rates in a cost-efficient manner. Here, we demonstrate the application of these carbon isotope, reaction-transport models to both steady-state and transient geochemical conditions in sediments located both in the shelf and in the slope.

ACOUSTIC SEDIMENT CHARACTERIZATION IN NEAR SEABED GAS ENVIRONMENTS AROUND THE IRISH COAST

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High frequency sonar systems have become the most widely used technique for seabed mapping in shelf and coastal areas worldwide, with the result that large volumes of data are now held in databases to be used in a variety of marine disciplines. Information derived from acoustic backscatter has potential applications in a wide range of marine areas, including the geophysical characterization of gas in shallow sediments. The relationship between gassy sediments and acoustic backscatter is complex and presents a non-linear character. Understanding this relationship, and its limitations, is critical to attempt any geophysical characterization in this type of media and to improve the description of common acoustic gas related anomalies. In this paper we present the results from a number of areas around the Irish coast, using a multiple approach analysis comparing a number of concurrent geophysical datasets in soft homogenous fine-grained gas-bearing substrate: from multifrequency single-beam time-series to multibeam angular range analysis (ARA), including shallow seismic profiles, marine conductivity measurements and sediment core scans.

We have analysed single-beam time series returns at two different frequencies and at a number of depth intervals below the seafloor. Near seabed gas reflectors have different responses depending on the wave frequency. The 38 kHz single-beam backscatter returns appear more sensitive to subtle gas related variations. At this frequency, generally, responses associated to free gas appear as scatterers decreasing the general amplitude returns; however, enhanced reflectors parallel to strata are correlated to higher levels of backscatter. Multibeam backscatter (95 kHz) ARA profiles in the near-range angular sector show a good level of correlation with the single-beam, and a distinct signature due to the volume inhomogeneities. The preliminary ARA results show good indices for differentiating between muddy facies and sandy dominated facies. Interestingly, the regions showing gas anomalous acoustic and conductivity signatures are generally correlated with areas adjacent to escape features, suggesting the gas in these regions is largely trapped in the sediment.

POTENTIAL RISK IDENTIFICATION FROM METHANE HYDRATE PRODUCTION: CASE STUDY INDONESIA

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During 1999-2005 the Indonesian potential gas hydrate have been reported during "incidental" exploration spread in offshore of Mentawai, Java fore-arc basins and deep water North Makassar basin. In year 2004, an "un mature" preliminary methane hydrate potential deposit calculation were found totally to be around 850 trillion cubic feet (tcf). Risk forecast using random generation is developed to identify the potential risk from gas methane hydrate production with case study of Indonesia. The tool is based on a simulation software and applied to find the dominant risk in production scenario of methane hydrate in offshore Indonesia. The five possible scenarios are studied base on impact: (i) thermal stimulation in which the temperature is increased through heating so that hydrates break into water and gas and the gas is recovered, (ii) depressurization in which the pressure is lowered by pumping out gas at the base of the hydrate that causes dissociation of hydrates into gas and (iii) chemical inhibitor injection where a dissociating agent like methanol is injected into the hydrated sediments that leads to the destabilization and releases gas from hydrates, (iv) fracking and (v) CO_2 injection.

The main strength of this risk assessment method is that it has a high probability of obtaining better solution with significantly fewer simulation runs than other methods. Also, by changing step size, it is possible to influence the results. This method is general and can be applied to other process modeled or activities. The result of this study can be applied in such production strategy decision considering the potential geo hazard, economic, optimal production, flow assurance and environment.

VARIABILITY OF CHEMOSYNTHETIC ASSEMBLAGES AMONG AND WITHIN POCKMARKS OF GULF OF GUINEA

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Several giant pockmarks of the Congo basin as well as smaller ones on the Gabon margin were revisited or newly explored with the ROV Victor 6000 during the WACS cruise (2011). Detailed bathymetry and video mosaics of the Regab pockmark located at 3170m, processed from the Victor multibeam and video data, and extensive sampling, complete the knowledge of this pockmark and the distribution of assemblages dominated by Bathymodiolin and vesicomyid bivalves, as well as siboglinid tubeworms. In the Kouilou area located at similar depth 100 miles to the north, the pockmark Worm Hole previously surveyed by deep-towed camera (Sahling
et al.2008) was confirmed to be colonised by Siboglinids and by few vesicomyids, but Bathymodiolid beds were also observed. The pockmark Baboon visited for the first time revealed extensive siboglinid tubeworm fields as well as bathymodiolids and vesicomyids. Finally the Guiness area located at 700m depth on the Gabonese margin is only colonised by scattered beds of vesicomyids and rare siboglinids. The differences observed in the faunal colonisation between pockmarks and the distribution of assemblages within the Regab pockmark are discussed on the basis of
methane concentrations above the seafloor, trace elements (Fe, Mn), chemistry of interface and interstitial waters, as well as distribution of gas bubbles, gas hydrates and carbonate concretions on the seafloor.

Reference
Sahling H, Bohrmann G, Spiess V, Bialas J, Breitzke M, Ivanov M, Kasten S, Krastel S, Schneider R (2008) Pockmarks in the Northern Congo Fan area, SW Africa: Complex seafloor features shaped by fluid flow. Marine Geology 249:206-225

Seafloor fluid emissions in the French Guiana passive transform margin (Demerara Plateau)

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Transform margins are characterized by an abrupt continent-ocean transition and a steep continental slope. They are also frequently affected by numerous submarine landslides and fluid-escape structures.
The eastern Demerara Plateau, located offshore French Guiana, corresponds to an indentation of the shelf. Multibeam bathymetry and backscatter imagery, 6-channel seismic data and 3–5 kHz echosounding acquisition was carried out along the Plateau in 2003 during the GUYAPLAC cruise.

We identified fifty depressions on the seafloor of the Demerara Plateau. Backscatter imagery data show that some of these depressions are highly reflective, suggesting they could be active pockmarks (Fig. 1). The elongation of those features could be due to deep-sea currents such as the DWBC (Deep Western Boundary Current). The distribution of the pockmarks within the field is heterogeneous. The pockmarks are characterized by widths varying between 100 m and 2 km, and lengths ranging from 100 m to 10 km. The depth of these structures ranges from 5 m to 90 m below the surrounding seafloor. Smaller pockmarks could be present.
Pockmarks, on 3–5 kHz echosounding data, appear as asymmetrical depressions (Fig. 1B). The upper flanks are associated with transparent facies corresponding to Mass Transport Deposits (MTD) or gas. The sediments affected by the pockmarks were sometimes subjected to gravitational instabilities.
Low resolution and relatively large spacing between the seismic profiles make pockmarks difficult to observe on such seismic data. The pockmarks generally develop above a MTD. However, some pockmarks lie above faults probably acting as permeable conduits.
The Cenozoic sedimentary cover of the Demerara region is densely faulted by sub-vertical normal faults (Fig. 1A). These faults, visible on NW-trending as well as on NE-trending seismic profiles, only affect the Cenozoic cover and have been interpreted as polygonal fault intervals.

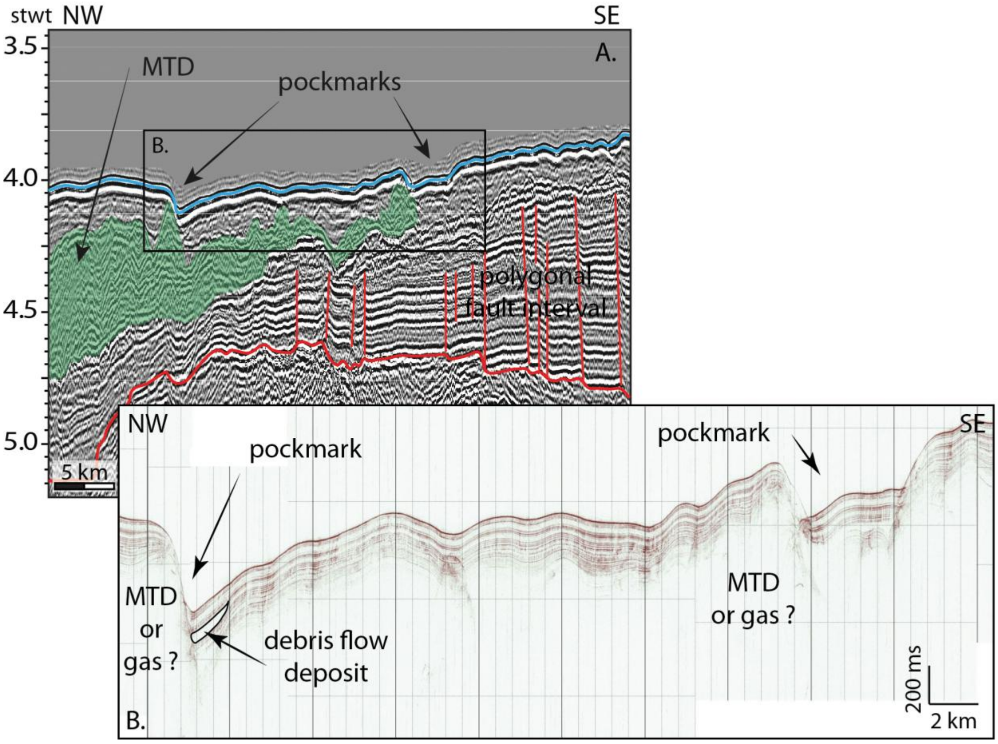

Figure 1: Pockmarks, polygonal fault interval and MTD's in the Demerara Plateau. A. Seismic profile (vertical exaggeration x5); B. 3–5 kHz echosounding profile.

The fluids could have a compactional, biogenic or thermogenic origin in the study area. We hypothesize that the compactional fluids could be coming from the MTD's which feed these pockmarks by dewatering or could be produce by the development of polygonal faults. The Black Shales of the Cenomanian are another potential source for the biogenic fluids. Data from ODP Leg 207 suggest that most of the gases could be generated by *in situ* microbial activity. Evidence for migration of presumably thermogenic methane has also been described in the ODP Leg 207. Recent discoveries have revealed the presence of hydrocarbons along the French Guiana margin (Zaedyus well). Furthermore, polygonal fault interval affects the sedimentary cover. The base of this interval is located on the Albian-Aptian unconformity. These faults could therefore be used as drains by the deep-origin fluids.

The sedimentary cover of the Demerara Plateau endures ongoing sliding. We suspect fluid overpressures and the specific “free border” architecture of transform boundaries to be key parameters in the development of wide MTD’s contributing to the erosion of the eastern Demerara Plateau.

AUTHIGENIC CARBONATES FROM THE CHEOPS MUD VOLCANO - MENES CALDERA (NILE DEEP SEA FAN-EASTERN MEDITERRANEAN)

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Active cold seeps associated to mud volcanoes and pockmarks are widely distributed in Eastern Mediterranean Sea. During fall 2007, the MEDECO cruise, onboard the « R.V. Pourquoi Pas ? », investigated different deep Mediterranean cold seep ecosystems using the ROV-Victor. Part of the time was devoted to detailed investigations of Menes "caldera" located at the North-western foot of the Nile deep sea fan margin; Menes caldera 50 m deep, corresponds to a 8 km in diameter.sub-circular depression lying at 3100 m depth. It includes several mud volcanoes more or less active as indicated by back-scatter imagery.

The active Cheops mud volcano was explored during three dives, one for precise bathymetry and imagery of the sea floor and two for various sampling and measurements; this structure has a diameter of about 400 m and culminates 30 m above the seafloor. Its top contains a muddy-brine lake about 400 m deep, surrounded by a circular rim from which the muddy brines are locally overflowing on the northern flank of the volcano. The CH_4 content of the brine is very high (2.44 to 3.74 mmol/L) and the salinity varies between 210 to 244 g/L.

Authigenic carbonate crusts covering the sea floor are relatively scarce and occur as light grey, thin and highly porous laminated crusts that may form small micro mounds; they are slightly more abundant and associated with polychaetes along the northern flank of the feature (Fig 1).

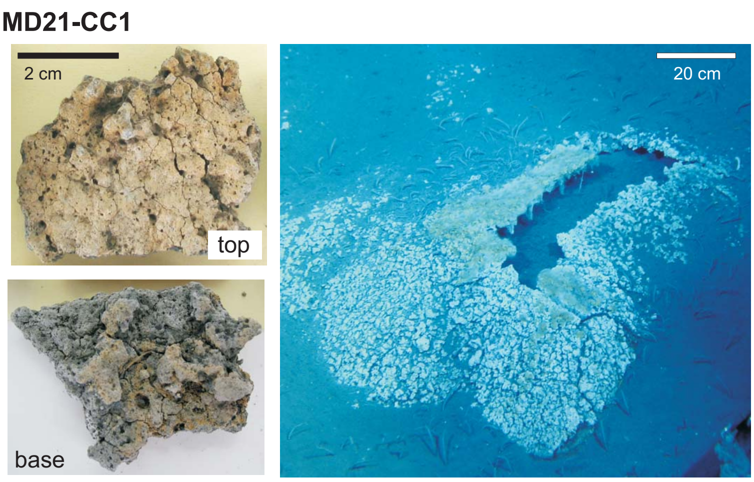

Figure 1: Macrofacies and seafloor view of carbonate crusts from Cheops mud volcano

Within the muddy brine lake, the authigenic minerals are represented by dolomite, ankerite, pyrite and barite (Fig 2A) whereas the sea floor crusts are made of mixtures of aragonite and magnesian calcite (Fig 2B); pyrite is always present as framboids or isolated octahedrons or cubic crystals. It is also interesting to notice that the aragonite crystals of the crusts include particles from the sedimentary matrix (as coccoliths); they also display numerous dissolution cavities that are interpreted as the result of aerobic oxidation of methane within the oxygenated bottom water.

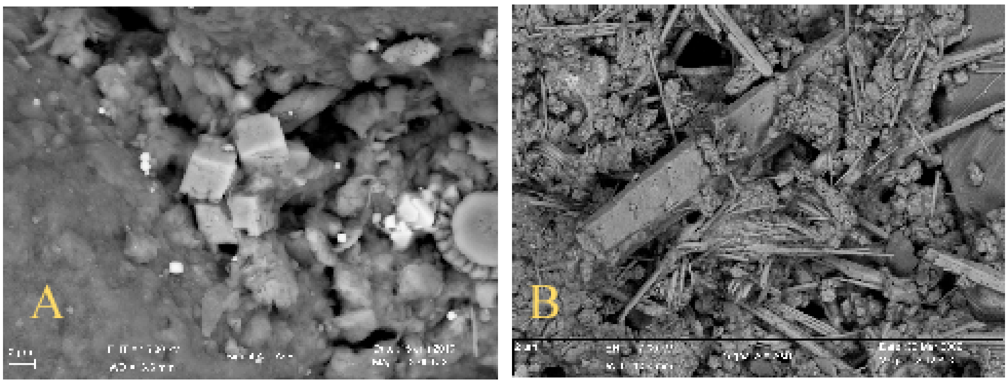

Figure 2: Cheops mud volcano: A – SEM observation of the mineral components (rhombs of ankerite, pyrite crystals) from the muddy brine; B- SEM observation of a carbonate crust composed of elongated crystals of aragonite (some with dissolution cavities) associated with clusters of rhombohedral crystals of magnesian calcite.

The oxygen and carbon isotopic compositions of bulk carbonate display very small variations (+2.91 < $\delta^{18}O$ ‰ V-PDB < +3.17; -42.58 < $\delta^{13}C$ ‰ V-PDB < -42.29). The $\delta^{18}O$ values fall exactly within the range of the equilibrium values calculated for aragonite (+3.3 ‰) and magnesian calcite (+2.9‰) precipitated with the present-day Mediterranean bottom water. The very low $\delta^{13}C$ values indicate clearly that the authigenic carbonate is derived from anaerobic oxidation of methane. Similar conclusions were proposed by Gontharet et al (2007) from their analysis of carbonate crusts previously recovered during the Nautinil expedition on Mykerinos, Chefren and Cheops mud volcanoes within Menes caldera.

Reference :
Gontharet S, Pierre C, Blanc-Valleron MM, Rouchy JM, Fouquet Y, Bayon G, Foucher JP, Woodside J, Mascle J, the Nautinil scientific party, 2007. Nature and origin of diagenetic carbonate crusts and concretions from mud volcanoes and pockmarks of the Nile deep-sea fan (eastern Mediterranean Sea). Deep Sea Research II, 54, 1292- 1311

This work has been supported by the European programs HERMES and HERMIONE.

PRELIMINARY ESTIMATE OF DISSOLVED COMPONENTS FLOWING THROUGH WATER-BOTTOM INTERFACE AT SITES OF OIL AND GAS DISCHARGE IN LAKE BAIKAL

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Baikal is known to be a deep-water lake which makes experimental measurement of diffusion flow from bottom sediments difficult. It is more likely to estimate relative value of a “possible” component flow going through the water-bottom interface according to Fick's First Law (Granina et al. 2005).

Surface sediments in South Baikal, at sites of shallow-water seeps Babushkin and Goloustnoe, and mud volcanos Peschanka-1 and Peschanka-2, are observed to have fresher bicarbonate waters compared to Baikal water, hence, component flows here are positive and directed from water to sediments. Most flows have been registered for bicarbonate ions, 410-640 mg/m^2 per day.

Near Posolskaya Bank gravitated toward delta of the Selenga River along the Posolsky Fault, there is a discharge of waters with increased mineralization that are mainly enriched in sulphate, bicarbonate, and calcium ions. These components have significant flows (up to -8000 mg/m^2 per day) and directed from sediments to water. Near the structure St. Petersburg, all studied components show negative flows. Maximum flow (-2500 mg/m^2 per day) is registered for bicarbonate ions. Kukui Canyon is located near delta of the Selenga River opposite to Posolskaya Bank. Here, in sediments of mud volcanoes, discharge of both bicarbonate and sulfate waters of significant mineralization takes place, thus, complying with extremely increased flows (up to -7000 mg/m^2 per day) from sediments to water.

The sites of oil discharge in Central Baikal have shown the highest flows for all components, because oil-associated waters have the most diverse content of ions and mineralization. Maximum flow of bicarbonate ions and sodium ions from sediments to water have been detected at the site of hydrothermal discharge Frolikha Bay (-10 200 and -1600 mg/m^2 per day). Considerable negative values of flows have also been obtained for other components; it complies with an intensive inflow of mineralized waters of hydrothermal vent. It should be noted that at almost all sites high negative flows of bicarbonate ions are associated with those of acetate ones giving evidence of their suggested participation in methane cycle.

Therefore, estimates of the dissolved components flowing through water-bottom interface show that they significantly enter the water column at sites of subaqueous discharge of oil and gas in the eastern border of Lake Baikal. The flows of components near the western border are not so high; however, they are positive and directed from water to sediments.

This work was supported by Integration Project SB RAS No. 82, Programme of the RAS Presidium No. 23.8.

MULTI-DISCIPLINARY INVESTIGATIONS OF GAS HYDRATES AND FLUID SEEPS ON THE NILE FAN

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We present interim results of an investigation of gas hydrates in relation to fluid flow and seepage on the Nile fan, offshore Egypt. The study is based on a) modelling of gas hydrate stability for modern and glacial stage conditions undertaken by OGS and JUB, b) re-examination of seismic reflection profiles acquired by OGS (in 1973) and Géoazur (1998-2002); and c) analysis of data acquired during the Géoazur-led APINIL campaign in 2011 (seismic reflection profiles, multibeam and sidescan seabed and water column data, geothermal measurements and sediment cores).

Seismic reflection profiles covering a range of frequency content provide evidence of a bottom simulating reflection (BSR) in water depths of c. 2000-2500 m on the central Nile fan, consistent with information available from exploration activities. The BSR approximately coincides with the base of the theoretical stability zone for methane hydrate (MHSZ), suggesting a hydrate occurrence zone up to 250 m thick. The seabed of the central Nile fan in depths of 1800-2500 m is characterised by numerous pockmarks, high backscatter patches up to 400 m wide that seabed observations have shown to correspond to authigenic carbonate pavements; the edges of some have been shown to be associated with gas seepage to the water column. Several pockmarks were investigated during APINIL, in depths of 2000-2200 m, resulting in hydroacoustic evidence of water column gas flares up to 600 m high. Cores acquired near two pockmarks indicate slightly elevated geothermal gradients and samples are being analysed for gas content. Pockmarks across the central Nile fan lie above the seismically identified BSR, indicating that gas is seeping upwards from or through the hydrate occurrence zone.

The MHSZ would have been up to 50% thicker during the last glacial stage due to cooler bottom waters (by up to 4°C), implying a marked reduction in gas hydrate stability on deglaciation; this could have resulted in increased gas pressures at the base of the stability zone. The Nile fan is characterised by recurrent slope failures, with up to 10 large-scale slides identified during the last glacial cycle, not all linked to sea level changes. Information on bottom water paleo-temperatures would facilitate an assessment of to what extent gas hydrates are driving both fluid flow and slope failure on the Nile fan.

Acknowledgements: Data from the Nile fan are being analysed in the context of the HYDRANIL project, a collaboration between researchers in Italy (OGS), France (Géoazur), Germany (JUB) and Brazil (PUCRS). Gas hydrate stability modelling was initially funded through the EU Marie Curie EIF project HYDRAMED at OGS.

Influence of hydrophobicity on the performance of inhibitors for carbon dioxide hydrate formation

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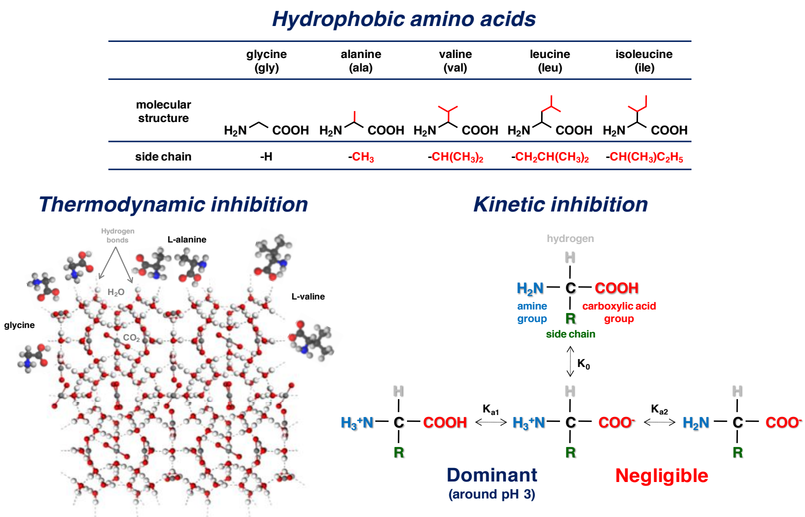
Carbon dioxide has been regarded as highly risky one among various gas components in flow assurance because it is acidic when dissolved in water and forms clathrate hydrates under relatively high temperature and low pressure conditions. In response, hydrate inhibitor injection is one of the promising technologies to prevent pipelines from plugging. Despite a great deal of effort during decades, fundamentals on hydrate inhibition mechanism have not been fully understood yet. In this work, we suggest amino acids as new inhibitors and model system to investigate the inhibition mechanism. As thermodynamic hydrate inhibitors, carbon dioxide hydrate phase (liquid water-hydrate-vapor) equilibrium conditions with 3 hydrophobic amino acids (glycine, L-alanine, L-valine) were measured in the temperature and pressure range of 273.05-281.45 K and 14.1-35.2 bar. By comparing their inhibiting effects, we confirmed that the thermodynamic inhibition is driven by “hydrogen bond” and “hydrophobic effect”. Along with these results, as kinetic hydrate inhibitors, the nucleation and growth kinetics of carbon dioxide hydrates with 0.01-1.0 mol% injection of 5 hydrophobic amino acids (glycine, L-alanine, L-valine, L-leucine, L-isoleucine) were measured by constant cooling and isothermal method. In this case, the opposite trend was seen in the hydrophobicity dependence of amino acids on kinetic inhibition performances. The main reason why amino acids delay the hydrate nucleation and reduce the growth rate is expected to be caused by the formation of zwitterions in water. Furthermore, microscopic measurements for carbon dioxide hydrate with amino acids were carried out for the spectroscopic identification. One distinct advantage of the application of amino acids as inhibitors is their environmentally friendly nature. It may, therefore, lower the damage to the environment significantly. Also, the recovery cost can be considerably reduced because amino acids are nonvolatile.



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THE BERING SEA BASIN: NEW DRILLING AND GEOPHYSICAL OBSERVATIONS AND EVIDENCE FOR AN IMPORTANT CONTRIBUTION OF THERMOGENIC METHANE TO INTERSTITIAL DEPOSITS OF METHANE HYDRATE

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ASCENDING THERMOGENIC METHANE BENEATH THE BERINGIAN CONTINENTAL MARGIN

In 2009, IODP Exp 323 drilled three sites (U1343 at 1951 m, U1344 at 3172 m, and U1345 at 1007 m) along the Beringian margin of the Bering Sea Basin to recover the late Cenozoic paleoceanographic and paleoclimatic history stored there (Figs 1A and B). Warming sediment cores vigorously released methane gas, implying dissociation of pore-space methane hydrate, although hydrate was not visually seen. At a sub-seafloor depth of 350 m, a regionally extensive BSR was penetrated at Site U1343, and at 440 mbsf at the deeper-water setting of Site U1344 (Figs. 1C and D). P-T conditions at the BSR matched those of the phase transition from methane gas below to methane hydrate above (Figs. 1E). Below sectors of acoustically bright BSRs, seismic profiles recorded gas-blanking effects in wide columns (~1->3 km) that extended to sub-seafloor depths of 2-3 km (Figs 1C and D). These depths and the measured thermal gradient of ~53 deg C/km imply that methane generation at 2-3 km sub-seafloor is dominantly thermogenic. Exceptionally large submarine canyons cut through or deep into the margin's 2-7-km thick sedimentary pile. Canyon excavation provides venting outlets for deep-generated methane. Vertical migration of thermogenic methane likely serves to brighten near-surface BSRs, and, within the waters of the canyon heads, help sustain there one of the world's most prolific ecosystems.

ASCENDING THERMOGENIC METHANE BENEATH THE ABYSSAL FLOOR OF THE ALEUTIAN BASIN

In the 1970s and 80s, seismic reflection profiles of the 3-4-km-thick sedimentary sequence underlying the abyssal floor (3400-4000 m) of the Aleutian Basin revealed thousands of vertical columns of shallow up-arched reflection horizons overlying deeper down-bowed horizons. The maximum up-arched reflection was highly reflective and of reversed (negative) polarity. Its P-T setting implied it was a gas-hydrate BSR (Fig. 2B and D). These **v**elocity-**amp**litude anomalies, or VAMP structures, were hypothesized to be recordings of higher velocity sediment containing hydrate (velocity pull-up) overlying the top of a chimney of ascending low-velocity methane gas (velocity push-down) (Fig 2B). Cumulative downwarping increased with depth to at least 1.5-2.5 km, which is largely through Miocene and younger diatomaceous sediment. The deep-seated gas indicators, together with an estimated thermal gradient of ~60 deg/km, imply methane generation is dominantly thermogenic.

Definitive interpretation of what VAMP structures physically are has been hindered by the circumstance that none had been imaged by crossing seismic lines and no in-situ velocity data existed. These impediments were overcome in the summer of 2011 by the collection from the *R/V Langseth* of long-offset (8 km) MCS and companion OBS data.

The new data are presently undergoing initial study and interpretation. Preliminary processing by one of the authors (Wood) documents that at VAMP structures a volumetrically large, downward tapering mass of methane gas underlies the BSR and is responsible for the posited velocity push down (Fig. 2C, deep blues, purples and black). With velocity correction, the "downwarped" reflections on time-domain plots are revealed in true depth to be gently domed upward. Doming continues up section across the BSR and into overlying beds (Fig. 2D). Only a relatively thin section of high-velocity beds were detected above the BSR that might contain dense, pore-space deposits of methane hydrate (bright green at ~4000-4100 m on Fig. 2C).

The new data definitively document that large VAMPs rise above deeply buried (2-3.5 km) basement relief (i.e., knolls, seamounts, ridge, e.g. the Cyrano high, Fig. 2B) and also the existence of a basin-wide abundance of smaller chimney structures (Fig. 2B). Interpreting and verifying these new observations are the foci of renewed investigations into what VAMPs physically are, the processes forming them, and what determines their basinal settings.

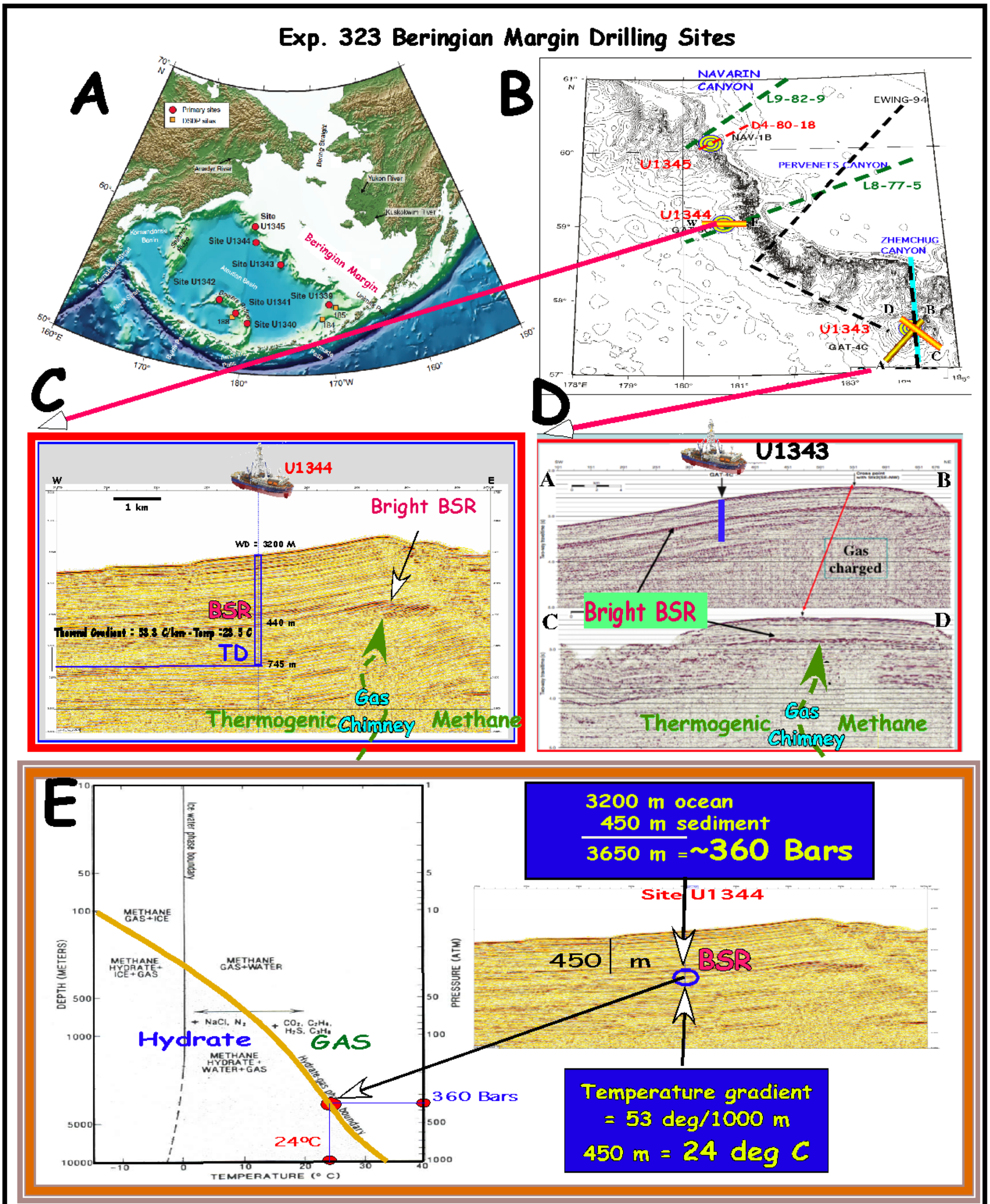

Fig: 1, Beringian margin BSR setting

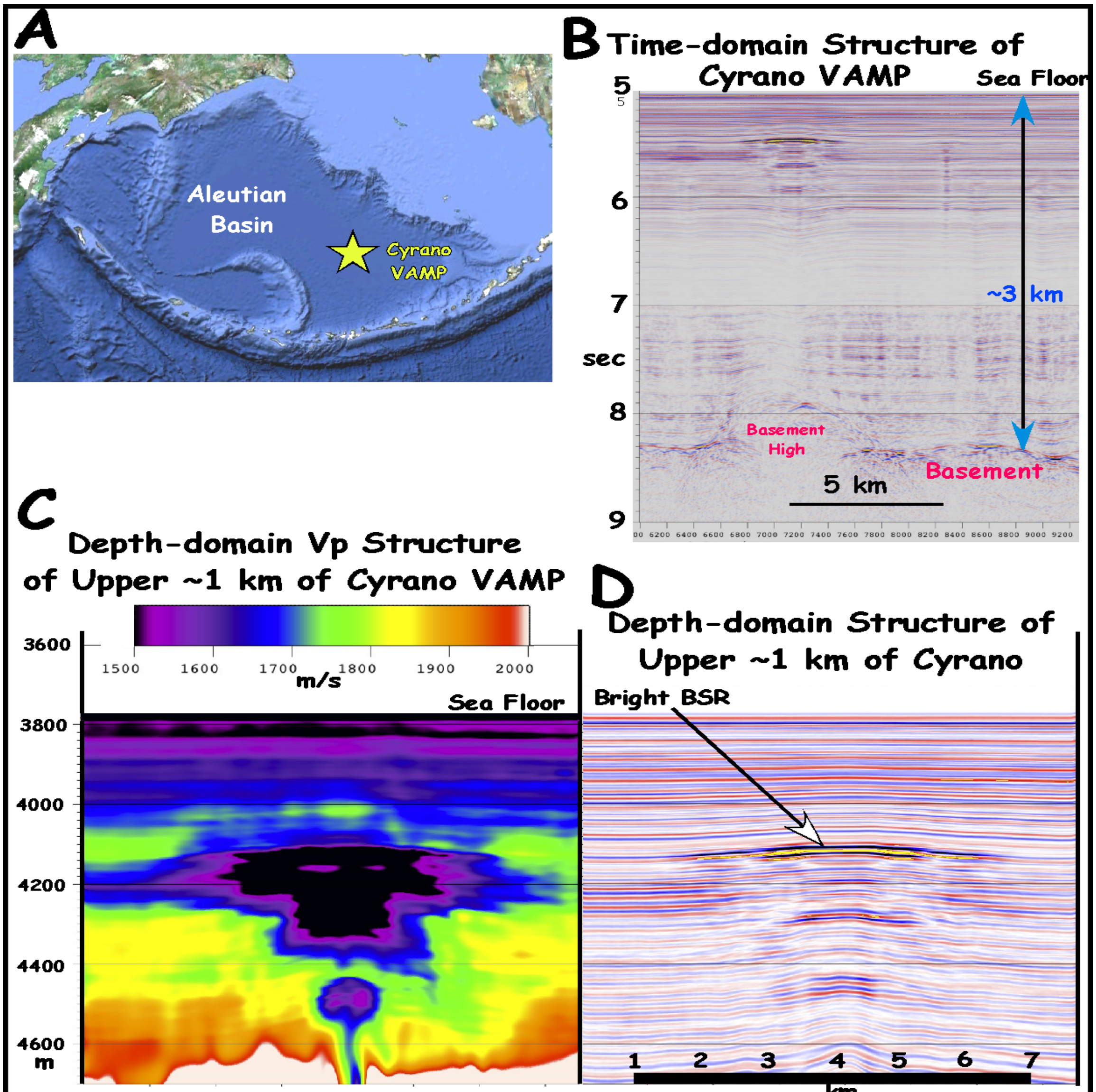

Fig 2: Depth-, time-domain, and Vp structure of Cyrano VAMP structure, Bering Sea.

INTERNATIONAL COLLABORATION EFFORTS OF SUBMARINE GAS HYDRATE STUDIES OFFSHORE SAKHALIN, OKHOTSK SEA

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Abstract

Gas hydrates are potential energy resources for the future and natural reservoirs of greenhouse effect gases. Methane hydrates exist beneath sea bottom near cold seeps NE off the Sakhalin in the OkhotskSea.Multidisciplinary field operations including various geophysical surveys and core analyses were performedto investigate seepage characteristics and gas hydrate formation mechanisms.Russian, Korean and Japanese researchers have been involved in the international collaboration efforts for gas hydrate investigations. CHAOS (hydro-Carbon Hydrate Accumulations in the Okhotsk Sea) project started in 2003, and grew to SSGH (Sakhalin Slope Gas Hydrate) project in 2007. One of the major outcomes of the projects is the findings of dense distributioncharacteristics of the near-bottom gas hydrates offshore NE Sakhalin in the Okhotsk Sea. Fifteen sites have been discovered for the near-bottom (shallow) gas hydrates within a submarine depth of 3 m in sea bottom coresas shown in Fig.1. The first shallow hydrate was found near Obzhirov Flare in 1991 by Russian scientists during the VNIIOkeangeologia and PO Dalmorgeologiaresearch cruise. The second hydrate was found near Gisella Flare in 2005 by Russian and German scientists during KOMEX cruise. Thirteen additional sites were found during the CHAOS and SSGH cruises. The shallowest hydrates were obtained at sites of very shallow water depth (DU, GI) or very large seepage structures (Obzhirov, KO) as shown in Fig.1.

Comprehensive study efforts have been continued to better understand the

formation mechanisms of gas hydrates by conducting collaborative field operations and laboratory analyses.

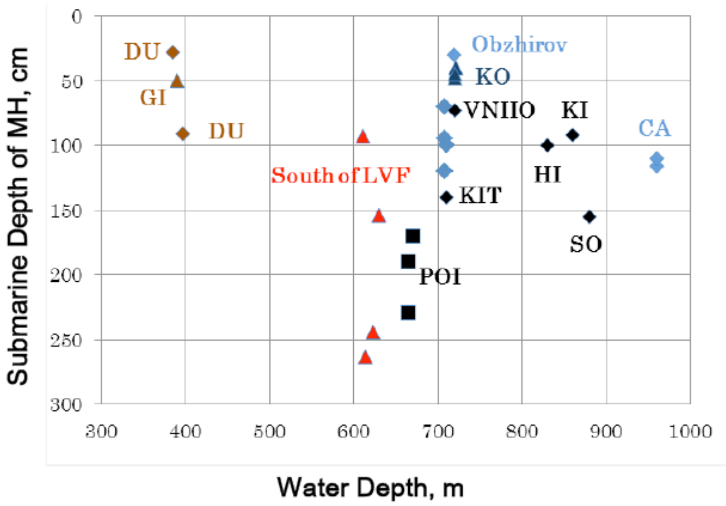

Fig.1 Methane hydrate-bearing cores obtained near sea bottom offshore NE Sakhalin (DU; Dungeon, GI; Gisella, KO; KOPRI, VNIIO; VNIIOkeangeologia, KI; Kitami, HI; Hieroglyph, CA; CHAOS, SO; Soloviev)

PECULIARITY OF GAS HYDRATE ACCUMULATION HISTORY CAUSED BY DIFFERENCE IN RHEOLOGICAL PROPERTIES OF MARINE SEDIMENTS

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Depths of hydrate stability interval and hydrate saturation are different in natural environment. While a position of gas hydrate stability zone (HSZ) in marine sediments depends on geothermal gradient and on pressure in sediments, hydrate saturation depends on a number of reasons, main of which is a gas supply into HSZ. An upward filtration of gas and gas-saturated fluids is recognized as a most powerful source of methane for forming gas hydrate in gas hydrate *PT*-stability zones in marine sediments (Davie and Buffet, 2002). So, in hydrate studies it is necessary to account the factors which determined the filtration rate. Upward filtration rate depends upon a gradient of pore fluid pressure, which is formed due to sediment compaction. Sediment compaction process is a complicated geophysical process which takes place during geological history of sedimentation. Compaction rate and, hence, filtration rate of pore fluid depend on physical, rheological, and by hydrodynamic properties of accumulated sediments and sedimentation rate (Suetnova and Vasseur, 2000; Suetnova, 2010), which may be different in natural environments. Effective viscosity and compressibility of sediments may vary in order of magnitude in dependence of lithology. In present study the influence of difference in rheological properties of marine sediment sheets on to history of gas hydrate accumulation is investigated by using the mathematical and numerical modeling. It is assumed that sediments move down through the hydrate stability zone (HSZ) during geological time of sediments accumulation and its burying. Schematic drawing of the model setup is shown at Fig.1. The processes of heating and compaction of growing sediment layer and filtration of pore fluid and gas hydrate accumulation in pore space in HSZ are related in the system of partial differential equations. The system of partial differential equations includes: Darcy's law; compaction equation based on poro-viscoelastic rheology of sediments; conservation (continuity) equations for fluid, sediments, and gas (including gas hydrate accumulation); energy low; appropriated boundary conditions (Suetnova, 2008). The decreasing of free pore space due to gas hydrate depositions is taken into account following (Suetnova, 2007). Scaling of the equations system leads to the emergence of important dimensionless coefficients which are the nonlinear combinations of physical parameters of sediments (Barenblatt, 1996). To reveal the dependence of hydrate saturation upon the rheological properties of sediments the number of model calculation were performed using geophysical data on known hydrate regions (Suetnova, 2008). The thickness of hydrate stability zone, c_h and the dependences of c_{eq} on *P-T* conditions were taken using results of Davie, Zatsepina and Buffet (2004). Gas hydrate accumulation was calculated for the three model cases, which was differed only in the rheological properties of sediments. The results of calculations are shown at Fig.2 in dimensionless form; corresponding basic parameters of sedimentation are summaries at Table 1. In present study it is compared the hydrate saturation resulting of 1,9 My history of sedimentation. Curve 1 presents the calculation results of hydrate saturation of pores in the case of basic value of sedimentation parameters. Curve 2 presents the calculation results of the hydrate saturation of pores in the case when sediments with relatively lower viscosity (two time smaller than basic value of viscosity) were accumulated after more viscous (basic value of viscosity) sediments during the dimensionless time interval 12,1 -24,6. Such dimensionless time interval is about of 1.My–1.9 My from the beginning of sedimentation. Curve 3 presents the calculation results of the hydrate saturation of pores in the case when viscosity of sediments is two time smaller than basic value of viscosity. All other parameters of sedimentation are equal to the basic values, listed in Table 1. Comparison of this curves obviously show that the gas hydrate accumulation rate and the resulting hydrate saturation increase with decreasing in effective viscosity of marine sediments. This peculiarity is manifested in curve 2 and 3 which correspond to smaller value of viscosity. These results outline the role of sediment rheology in the process of gas hydrate accumulation during sedimentation history.

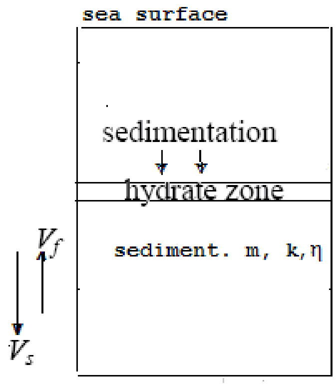

Figure 1. Schematic drawing of of the model setup.

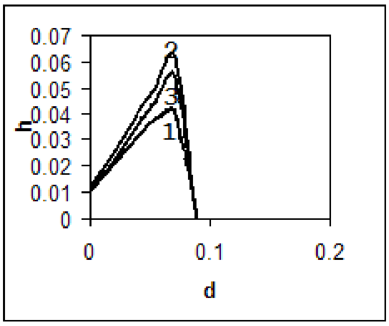

Figure 2. Comparison of calculated hydrate saturation versus distance from sediment surface d, normalized to sediment final thickness, resulting after 1,9 My of sedimentation. See text for notations.

Table 1. Basic parameters of sedimentation

Symbol	Parameter	Value	Units
V_1	Sedimentation rate	10^{-10}	m/s
m_0	Porosity	0,3	
η	Viscosity of sediment	$5 \cdot 10^{20}$	Pa s
μ	Viscosity of fluid	$2{,}6 \cdot 10^{-3}$	Pa s
ρ_f	Density of fluid	$1{,}0 \cdot 10^{3}$	kg/m^3
ρ_s	Density of sediment	$2{,}65 \cdot 10^{3}$	kg/m^3
β	Pore compressibility	10^{-9}	1/Pa
k_0	Permeability coefficient	10^{-13}	m^2

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METHANE DIFFUSIVE FLUX IN THE SHALLOW LAGOONS OF THE SE BALTIC SEA

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Curonian and Vistula shallow (mean depths are 4 and 3 m) lagoons are separated from the open Baltic Sea by the longest in the Baltic Sea sandy spits. Interconnection with open sea saline waters through narrow straights makes them intermediate basins, serve as collectors for fluid and hard land runoff. Marine conditions mainly dominate in Vistula lagoon; however river influence is high in the studied southern part of the Curonian lagoon. The sedimentation processes in both lagoons differ a lot: accumulation in Curonian and outflow in Vistula lagoon.

First attempt to study methane concentrations in these lagoons was taken in June 2011. Sediment (mud) and water cores were taken by hermetic corer (60 cm). Methane concentration was measured using "headspace analysis".

The difference in methane concentration of surface sediment layer (0-5 cm) and near-bottom water results in gas diffusive flux from sediment to water in spite of its microbial oxidation. Calculated using concentration gradient methane fluxes were various in the lagoons (Fig. 1). For Vistula lagoon CH_4 flux changed in range 0.1- 0.93 mmol m^{-2} day^{-1}, with mean value of 0.45 mmol m^{-2} day^{-1}. Curonian lagoon was characterized by 0.00-0.25 mmol m^{-2} day^{-1}, with mean flux of 0.07 mmol m^{-2} day^{-1}.

Low diffusive fluxes in Curonian lagoon may be a result of wind conditions when sampling was done. Stormy wind in the Curonian lagoon provided resuspension of the upper mud layers what led to methane escape to the near-bottom water. This supposition may be supported by two facts. Firstly, the methane concentration in the near-bottom water in Curonian lagoon at all points is for one order higher than in Vistula lagoon. Secondly, an additional calculation of methane flux for averaged concentrations for 0-10 cm sediment layer showed relevant values for both lagoons (0.1 and 0.11 mmol m^{-2} day^{-1}). Therefore stormy conditions provide volley methane escape from the mud to water resulted in heightened gas concentrations in the near-bottom water. It may be suggested that after moderate winds establishment methane began to accumulate again and lagoons became similar in flux.

As it was mentioned in a number of studies the diffusive flux in "sediment-water" border is higher during daytime due to temperature variations. That's why presented flux values can be overestimated. However, no gas escape by bubbling (its value can be considerable) was considered in this study. Adding "bubbling" flux to diffusive will increase the total amount of methane exchange in the near-bottom environment.

We understand that obtained results are only the first step in gas study in Curonian and Vistula lagoons and few measurements can't be used for methane budget calculation for the entire basins. So the additional future all-season monitoring observations are required.

This study was partly supported by RFBR 11-05-01093-a and 08-04-92422-BONUS_a.

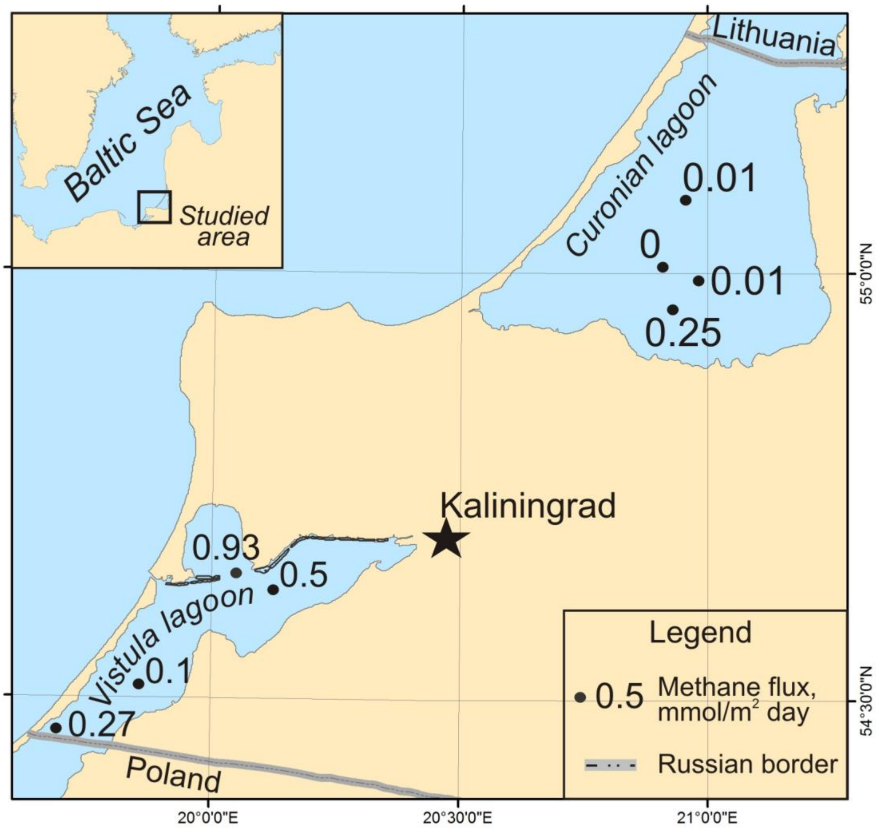

Fig. 1 Diffusive methane flux from the sediment to the near-bottom water in Curonian and Vistula lagoons, the Baltic Sea (June 2011).

SPATIAL DISTRIBUTION ANALYSIS AND HYDROACOUSTIC MONITORING OF A GAS SEEP AREA OFFSHORE SVALBARD (~ 78 N)

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The Arctic region comprises large and varied reservoirs of methane (from both terrestrial and marine sources). Gas hydrates within continental slope sediments or associated with permafrost underneath the Arctic shelves represent one of them. The stability of these hydrates is determined by environmental conditions (pressure, temperature) and changes in these conditions may cause the hydrates to dissociate and free gas to be released at the sea floor.

Methane gas emissions at underwater seep sites offshore Svalbard (W-Spitsbergen, ~78° N) have been associated with the decomposition of hydrates caused by the slow warming of the northward Atlantic waters (Westbrook et al., 2009). The seep site area discovered by Westbrook et al. (2009) has been revisited during a series of international surveys in 2009, 2010 and 2011, in order to detect and map the seep sites and monitor the activity of this phenomenon.

During the surveys, hydroacoustic data was acquired with multibeam and single-beam sonar systems. Data recorded with the scientific split-beam echosounder*SimradEK60* has been analyzed and processed to obtain physical parameters of the seep sites. A specialized graphical user interface created in Matlab (*FlareHunter*) was created and using the data of the spatial distribution inside the beam (electrical angles acquired with the split-beam method) 3D information was obtained of the backscattering pattern produced by the rising gas bubbles. Using this information, it was possible to find tendencies and accurate locations of each seep site. The tendency of the seep, herecalled "flare spine", could be reconstructed by applying a geometrical average to the 3D backscattering distribution of each flare. Locations of seeps from different echograms were compared in order to avoid overestimation of the number of flares. Also, flare positions were compared to know the spatial variability of the seep site area between the different years. In addition, information about bubble rising speed was extracted from the echograms. This information was compared with visual observations obtained with a video camera in order to obtain an estimation of the bubble size distribution (BSD) of the gas bubbles released at the different seep sites. Information of the average of the backscattering volume strength (S_v) of the seep site source was obtained as well.

Based on these physical parameters from our observations, a hydroacoustic method presented by Muyakshin et al. (2010) will be used in order to calculate the gas flux rates from the different seeps found.

By integrating all this information we aim to create a quantitative map of the bubble release in the study area.This will help to improve our understanding of the dynamics of the processes involved as a function of time and space, and to assess the potential of the released methane to reach the atmosphere and impact on climate change processes.

Spatial variation of the heat flow and BSR on the south-central Chilean forearc.

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In subduction zones, fluids are suspected to play a major role in the nucleation and rupture propagation of earthquakes. One of the world's most seismic countries is Chile and the southern Chile earthquake on the 22nd of May 1960 (Mw=9.5) was the biggest one recorded until present. Most of its seismicity is related to subduction, including the south-central area, where the 2010 earthquake (Mw=8.8) took place.

The thermal control of the rupture extent on subduction thrusts is especially important for estimating the hazard of great earthquakes where there have been no historical events. Heat flow (q) measurements on the surface of an active subduction zone and accretionary complex provide a critical boundary condition for the assessment of heat sources, but the quantity of data from in situ measurements in Chile is not well developed. For this reason it is necessary to assess the Earth's heat flow using other methodologies for a better understanding of the thermal structure in the Chilean margin.

In addition, gas hydrates occur worldwide in sediments beneath continental slopes and island arc's margins. The occurrence of gas hydrates in nature is controlled by an interrelation among temperature (T), pressure (p) and composition. A prominent feature detected on seismic surveys across some continental margins is the bottom-simulating reflector (BSR), which marks the base of the gas hydrate stability zone. Because the occurrence of gas hydrates is controlled by p-T conditions, it has been used to estimate the heat flow through continental margins, using the following formula:

$$q = k\,(T_{BSR} - T_0) / (Z_{BSR} - Z_0)$$

with k: average thermal conductivity between Z_{BSR} (BSR depth) and Z_0 (seafloor depth).

In this study, we have identified the BSR in almost 80 seismic lines, obtained from seven different cruises offshore south-central Chile, between Valparaíso (~33°S) and the Chile Triple Junction (~46°S).

The objective is to assess the thermal state of gas hydrate bearing sediments, which have been seismically imaged in the research area between depths of ~70m to ~700m beneath the seafloor. Moreover, we used in situ temperature of the seafloor and conductivity data obtained from CTD (NOAA World Atlas), ODP Leg 202 and 141, respectively, along the accretionary wedge to have a better quality in our heat flow calculations.

We assume that one factor that controls the average heat flow along the forearc is the age of the subducted Nazca plate. Our results of BSR-derived heat flow show values from 35 to 70 mWm^{-2} in the north-center part of the study area and higher than 250 mWm^{-2} in the southern part close to the Chile Triple Junction. These results are consistent with the age of the subducted slab, because in the triple Junction there is roughly new crust (0 Ma and with high heat production) and it is aging to the north up to ~38 Ma (therefore colder) at latitude 33°S off Valparaiso. In the southern part, the high values of q could be controlled by the residual heat from the Chile Ridge, where new oceanic crust is created.

Moreover, we noticed that the heat flow varies not only along the forearc, but also across it. It has been proposed that this might be related with a shallower source of heat produced by fluids flowing through faults and fractures. Most results close to the trench tend to support a heat transport originated from a deeper structure, which might control the advection of heat into the subduction zone by the downgoing plate. However, landwards the results show in some parts larger variations: we noticed lower values in the younger accretionary wedge close to the trench changing landwards into higher values. These outcomes could also be related to a continental control linked to a radiogenic heat production.

Finally, we observed a curious distribution-pattern of the BSR along the forearc: from north to south there can be seen deep, discontinuous and blurred spots presenting itself upslope, changing gradually in a continuous, shallower and strong BSR located near the trench.

SEISMIC AND ACOUSTIC INVESTIGATION OF ACTIVE GAS SEEPAGE SITES CONTROLLED BY SALT TECTONICS IN THE LOWER CONGO BASIN

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The continental margin in the Lower Congo Basin is characterized by large Aptian salt deposits as well as large-scale sediment input from the Congo River. Active salt tectonics led to prominent deformation of the overlying sediment column including rafting and extensional movements upslope as well as compressional settings at the seaward salt edge.

We investigated the sedimentological and tectonic setting of two active methane seepage sites on the lower continental slope in the Lower Congo Basin using multichannel seismic data in conjunction with water column and sediment echosounder as well as bathymetric data.

Distinct seafloor ridges at the western termination of the salt province on the lower slope show the effects of compressional salt tectonics and its impact on overlying sediments. Biogenic and potentially also thermogenic gas from different source layers is able to migrate towards the seafloor due to the salt-induced deformation.

The data revealed that seepage in the study area is focussed on top of the topographic ridges and is caused by the leakage of gas from Miocene channel deposits in diapir-bounded small sedimentary basins. These host rocks are connected to the seafloor by tilted Miocene strata resulting from salt-induced deformation. That deformation leads to the breaching of Post-Miocene hemipelagic slope sediments that form an effective seal in the area. Multichannel seismic data show the accumulation of gas at the bottom of the gas hydrate stability zone within Miocene deposits as well as gas hydrates beneath the active seepage sites. Large bowl-shaped depressions at the seafloor show authigenic carbonates, seep-related biologic communities and gas bubble streams escaping from the seafloor.

Observed active seepage occurs close to the deformation front but is limited towards older areas of deformation upslope. Active large-scale deformation including breaching of the hemipelagic seal thus promotes seepage at the deformation front. However, similar deformation within the compressional regime further landward does not result in observable active seepage. Investigated seepage indications at a distance to the deformation front such as authigenic carbonates, backscatter and topographic anomalies were attributed to ancient seepage activities.

The restriction of active seepage to the deformation front is explained by the youngest deformation features creating pathways for methane from previously untapped biogenic reservoirs to the seafloor. Advanced diapir evolution resulting in the presence of near-surface salt may also hinder upward migration of gas by blocking pathways along strata, creating classical hydrocarbon traps.

GAS COMPOSITION OF CORED SEDIMENTS FROM GAS HYDRATE POTENTIAL AREA OFFSHORE SW TAIWAN

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The widely distributed BSRs imply the existence of potential gas hydrates in offshore southwestern Taiwan. To better constrain the gas sources in this area, in total 22 cores have been collected from different tectonic environments in offshore SW Taiwan during the r/v Marion Dufresne 178 cruise, including 17 giant piston cores, 4 CASQ box cores, and 1 gravity core. The results show that the major gas is methane with very few ethane and carbon dioxide. It indicates they are mostly biogenic source in origin. However, some gas samples from active margin do also exhibit heavier carbon isotopic compositions, which range from -40 to -60 permil and are similar with the gas composition of inland mud volcanoes of SW Taiwan. It implies that there is also thermogenic gas source in this region. Combined with previous data in this area, some results can be summarized as followings: (1) samples collected from lower slope of active continental margin exhibit very light carbon isotopic composition of methane which mainly generating by microbial activities ($\delta^{13}C$ = -72.8 ~ -112 ‰); on the other hand, methane from samples collected from upper slope of active continental margin is much heavier, indicating a thermogenic source ($\delta^{13}C$ = -45 ~ -63.8 ‰). (2) The lightest $\delta^{13}C$ value of methane and DIC observed at the SMI depth along the profile shows that carbon cycling within this transition indeed exists. (3) $\delta^{13}C$ profile of DIC in many sites become heavier with increasing depth; this indicates that CO_2 reduction become more and more important. These findings suggest that significant microbial activities occur in the study area.

Abstracts of poster presentations
(alphabetic order)

A NEW DIATOM SPECIES WITHIN THE SEDIMENTS OF A POCKMARK ALONG THE NORTH ANATOLIAN FAULT (MARMARA SEA).

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The Marmesonet Cruise onboard R/V le Suroit, exploring the North Anatolian Fault, encountered a pockmark structure, 150 m wide, with methane bubbles escaping from its flat bottom. The MET09-GR02 cored 4.6 m of sediments in this structure, with many carbonate concretions levels and disseminated carbonate crystals.

The presence of abundant *Braarudosphaera bigelowii*, usually conspicuous at the transition between marine and lacustrine sediments in the Sea of Marmara, was not found in the smear-slides of GR02. However diatom-rich levels are present between 44 and 344 cm, and one of the diatom encountered in great number is a new species.

This new fossil diatom with a raphe-bearing keel and a junction line in the strongly bilobated wings is described as *Entomoneis aureasini* Pailles & Blanc-Valleron sp. nov. It is particularly remarkable by valves resembling donkey ears that interconnect suggesting a chain/planktonic life style.

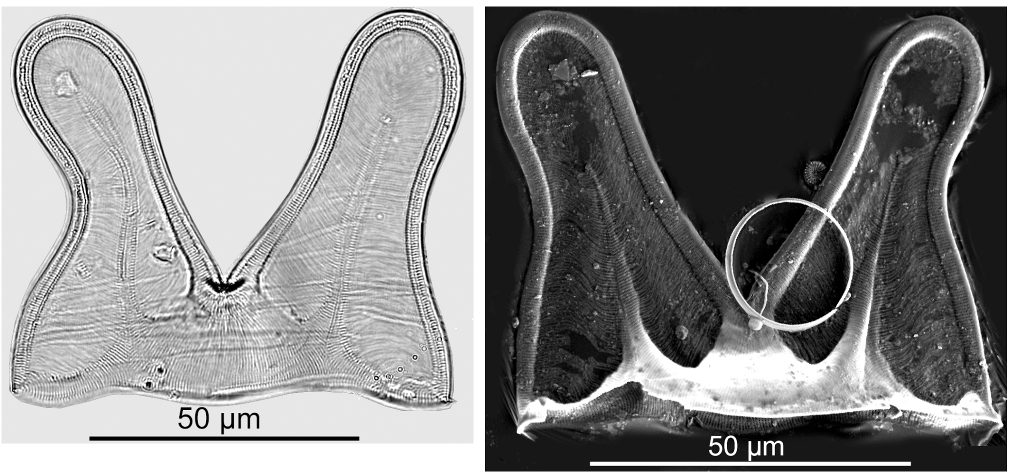

Fig.1: girdle view of the valve (left: optic microscopy, right: SEM).

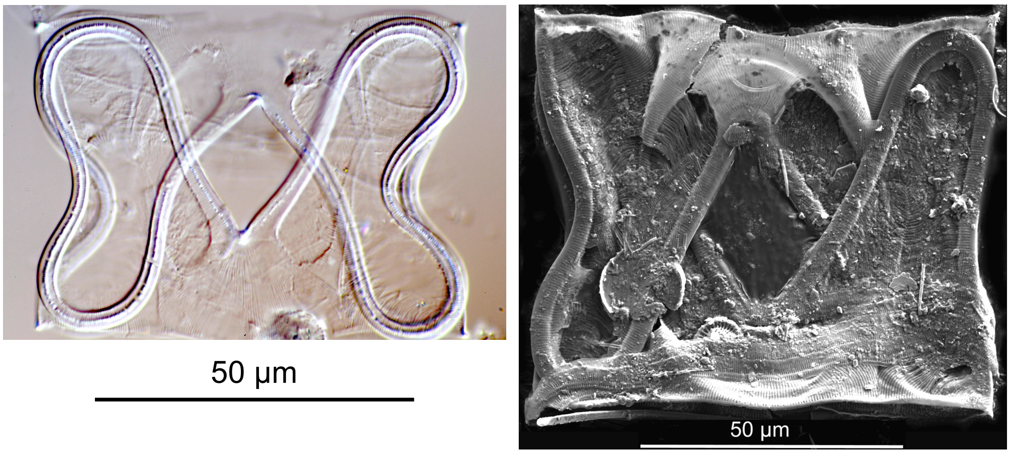

Fig. 2: valves of two different frustules, interconnected (left: optic microscopy, right: SEM).

The examination of sediments from other Marmara Sea cores sampled during Marmesonet 2009 and Marmara 2010 cruises show scarce *Entomoneis aureasini* in the upper lacustrine sediments but no bloom levels as in GR02.

METHANE CONCENTRATION AND SULFATE-METHANE TRANSITION IN SEDIMENTS OF THE SOUTHERN GDAŃSK BASIN (BALTIC SEA)

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The Gdańsk Basin (southern Baltic Sea) can be characterized as a region with organic-rich muddy sediments – TOC content > 4 wt % in sediments below the isobath of 60 m (Szczepańska and Uścinowicz 1994), anoxic/hypoxic zones in bottom waters – mainly in the area of the Gdańsk Deep and central part of the Gulf of Gdańsk (Łysiak-Pastuszak and Drgas 2004) and intensive primary production – frequent algal blooms due to nutrient enrichment from the Vistula river (Witek et al. 1997). The process of organic matter decomposition in such environments leads to methane production in the sediments (Claypool and Kvenvolden 1983). Before 2009, the Polish part of the Gdańsk Basin had not been geochemically investigated for methane occurrence in the sediments and thus the objective of the present study was to determine methane concentrations and the depth of sulfate-methane transition (SMT) in sediments from different areas of the Gdańsk Basin.

Sediment cores were collected in November 2009, March and September 2011 from seven stations located in the region of the southern Gdańsk Basin: central part of the Gulf of Gdańsk (stations 2.2, 5.1 and 5.4), Gdańsk Deep (stations 2.3 and 4.5) and Puck Bay (stations 4.1 and 4.3) by the means of a Niemistö gravity corer and a Rumohr Lot corer. Sediment samples were analyzed for: methane concentration, total carbon (TC), total organic carbon (TOC), total nitrogen (TN) and pore waters were investigated for: total alkalinity, sulfate, hydrogen sulfide and ammonium concentrations. Temperature, salinity and dissolved oxygen were additionally measured in near-bottom water.

Methane was reported in sediments of six stations and its concentrations varied from several dozen μmol dm^{-3} (St. 4.5) up to over 9 mmol dm^{-3} (St. 5.1). The highest values were observed in the central part of the Gulf of Gdańsk: > 1 mmol dm^{-3} already at 15-20 cm below the sediment surface and increasing up to about 6 – 9 mmol dm^{-3} at 50-100 cm bsf. Only slightly lower concentrations were observed in sediments at stations located in deeper parts of the outer Puck Bay (St. 4.1 and 4.3). Methane was not detected at St. 2.3. The values of TOC in top 10 cm of sediment cores were about 5.5 – 7 wt % at all the stations except for St. 5.1 (3.5 – 4 wt %). Our investigations showed that SMT was located very shallow within the sediments of the sampling stations: 10-15 cm at St. 5.1 and 5.4, and 15-25 cm at St. 2.2, 4.1 and 4.3.

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A SIMULATION STUDY OF EROSION AT GRANULAR AND PORE SCALES IN MARINE SEDIMENTS USING COUPLED LBM AND DEM CODES

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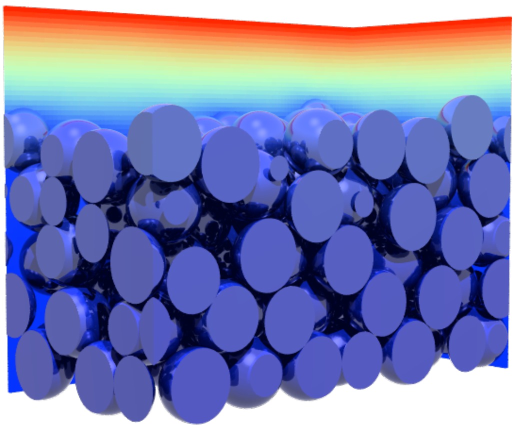
Abstract
The extraction of natural gas from marine sediments poses many engineering challenges. The focus of this work is on the issue of excessive sediment erosion. This is problematic as it may cause blockages around extraction wells, due to the build up of eroded particulate matter, reducing process efficiency. Thus, the motivation for this work is to determine the limits of safe operational fluid velocities and pressure gradients, as functions of sediment properties. The erosion of cohesive marine clays, subjected to shearing flows, is simulated using coupled lattice Boltzmann method (LBM) and Distinct Element method (DEM) codes. At a granular scale, individual clay particles, approximated as perfect spheres, interact with the fluid, and each other. Together, these particles are representative of a section of a bed of particles exposed to shear flow conditions. This shear flow is imposed via a moving wall, with a fixed velocity, placed at the system's upper most boundary. Particle-particle interactions are handled via the DEM code, while the LBM code, using the immersed boundary method, covers the fluid-particle force calculations.



A snap-shot of a system of 100 particles. The system has periodic boundaries in the x and y axes. Flat and featureless walls are positioned at the upper and lower z boundaries. The upper wall has a fixed velocity in the x axis, while the lower wall is stationary. The colours indicate the fluid velocity, with red being regions of highest velocity and blue the lowest.

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CARBONATE CONDUITS LINKED TO HYDROCARBONS ENRICHED SEEPAGES

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A current project presented here is focusing on modern and ancient carbonate conduits recovered in different geologic contexts such as the Plio-Pleistocene Northern Apennine foothills, the late Miocene Crotone basin (Calabria), the modern Adriatic Sea and Gulf of Cadiz. These poorly known methane-derived carbonates can be in principle useful for exploration as indicators of hydrocarbons reservoirs.
The project will integrate petrographic, geochemical and biomarker characteristics of chimneys and embedding country sediment within a precise stratigraphic and structural framework to better understand the genetic processes backing chimney formation.
In general, natural fluid seepages occur in a wide range of marine and terrestrial geodynamic settings. Tectonic context coupled with the evolution of the sedimentary systems play a major role in triggering fluid migration up to the surface. The recognition of fluid migration in marine environments is documented by a variety of morphological features ranging from ridges and mounds to depressions and craters, up to a mud volcanoes of considerable size. On land, the dominant geomorphic feature is represented by mud volcanoes. The hydrocarbon-bearing seepages can be associated with authigenic carbonate slabs and crusts, fluid conduits and chimneys. Mineral precipitation, above all authigenic carbonate precipitation, is often mediated by microbiological processes.

CARBON AND HYDROGEN ISOTOPE AND RELATED BIOGEOCHEMISTRY FROM GAS HYDRATE POTENTIAL AREA OFFSHORE SW TAIWAN

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In previous studies, high methane flux in offshore SW Taiwan was considered related to the dissociation from gas hydrate. However, dynamic microbial activities have been observed in the shallow sediments indicating mixture of methane from these shallow reactions. In this study, piston cored samples were collected from the studied area during several surveys since 2007 (r/v ORI, Leg 828, 835, 860 and r/v Marion Dufresne 178 cruise). The $\delta^{13}C$ of dissolved inorganic carbon (DIC) and methane and the δD of methane and interstitial water of cored samples were measured in order to identify the source of methane gas and biogeochemistry processes.

We can have following conclusions based on the results of this study. (1) methane gas of samples collected from lower slope of active continental margin are mainly generated by microbial activities ($\delta^{13}C$ = -60 ~ -112‰); on the other hand, methane gas from upper slope of active continental margin is mainly from thermogenic source ($\delta^{13}C$ = -45 ~ -63.8‰). (2) The lightest $\delta^{13}C$ value of methane and DIC usually occur at the sulfate methane transition zone (SMTZ) of depth profile, indicating that carbon cycling within this transition zone indeed exists. Thus, we can conclude that the ^{13}C-depleted methane could be generated at the top of methanogenic zone when the ^{13}C-depleted CO_2 produced by the microbially-mediated process of anaerobic oxidation of methane (AOM), and it may be recycled back to methane pool by the process of CO_2 reduction. (3) The δD of methane and interstitial water infer that CO_2 reduction could occur at SMTZ. (4) $\delta^{13}C$ values of DIC become heavier with increasing depth in many sites, indicating that CO_2 reduction process became more important at the depth of the profiles. All thèse evidences indicate that significant microbial activities in the studied area. Therefore, methane from microbial activities should not be overlooked in high methane flux area, even at gas hydrate potential area.

ACTIVE MUD VOLCANOES AND GAS SEEPS IN THE NEAR SHORE OF SW TAIWAN

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ABSTRACT

Multibeam echo sounder, EK500 sonar, deep-towed sidescan sonar and sub-bottom profiler surveys were carried out in the near shore area off SW Taiwan. High-resolution sub-bottom profilers and EK500 echo sounder data show the existence of a pockmark, more than one hundred gas seeps in sediments and ten gas plumes in water column in the study area. Thirteen mud volcanoes are recognized from the multibeam bathymetry. These mud volcanoes are located above mud diapiric structures. It indicates that the formation of each mud volcano is related to a mud diapiric structure. The fluid of mud volcanoes comes from the diapiric structures and migrates upward along fractures to the seafloor. For the first time, we have conducted a ROV survey for mud volcano observation in the near shore area off SW Taiwan in 2011. The results of ROV observation allow us to identify three active mud volcanoes with gas eruptions from seafloor. The eruption cycles for mud volcanoes MV1 and MV5 are about 3~8 minutes, and for MV12 is about 3~10 seconds. The high methane concentrations (100~550 nL/L) of seawater have been detected in the water column above the mud volcanoes, which is much higher than the average seawater value (< 50 nL/ L), implying a high methane flux beneath each mud volcano. Seafloor photos taken by the ROV and the deep-towed camera (TowCam) system show authigenic carbonates and chemosynthetic communities (bacteria mats and shells) on the seafloor, which also indicates a high methane flux in study area.

KEYWORDS: sidescan sonar, sub-bottom profiler, mud volcano, ROV, SW Taiwan

GEOPHYSICAL CHARACTERIZATION OF A GIANT FLUID PIPE IN THE NORWAY BASIN

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A giant fluid seep structure called the Giant Gjallar Vent (GGV) is observed on the Vøring margin, offshore Norway. The Vøring margin is affected by several rifting episodes, which formed the Vøring Marginal High, the Vøring Basin, and the Trondelag platform (Ren et *al*., 2003).

The break up is dated at 55 Ma, at which time widespread basaltic volcanism occurred in the area, emplacing numerous magmatic intrusions. Sills cover an area of 80000 km² at least in the Vøring and Møre basins (Svensen et *al*., 2004). During the Oligocene and Miocene, the formation of the Mogdunn and Helland Hansen Arches is linked to tectonic inversion (Chand et *al*., 2001).

We observed many mounds at the top of Intra Oligocene horizon (Planke et *al*., 2005). These mounds have a roughly circular shape with diameters on the order of 1 to 3 km. This horizon is shaly, likely impermeable and may allow accumulation of gas or other fluids underneath.

Exploration 3D seismic data (1996) permit to observe the Giant Gjallar Vent as well as several polygonal fault systems (Cartwright, 2011) between the Intra Oligocene and Top Kai horizons (0.01 Ma).

The Giant Gjallar Vent is characterized by a positive relief (ca. 15 m) at the seafloor level (Gay et *al*., 2012, in press). It is associated with three mounds at the Top Kai level: the east, west and central mounds. High amplitudes are observed beneath Top Kai horizon.

A seismic survey acquired in May, 2012 (RV Meteor, M87/2, Geomar, Chief Scientist: Prof. Dr. Christian Berndt) allows to constrain the GGV structure with 2D seismic, bathymetry and parasound data. The aim of the cruise was to know if the GGV is still active, and what sort of fluid lies beneath the Top Kai Horizon.

The new data have a significantly higher resolution than previous dataset, allowing seeing the structure, texture and morphology of the seafloor and 100 m below in far greater detail.

Preliminary results (in progress):

The GGV is centred on 2 chimneys with a height of 600 m and a diameter of 330 to 730 m separated by approximately 1300 m (Figure1).

The GGV is roughly elliptical in map view, with a long axis of 5 km and a short axis of 3 km. The 3D view shows these 2 chimneys are located beneath the central mound (Figure 2).

Seismic datasets show faults between the Top Kai and seafloor horizons. Above these faults, there is an amplitude increase at the seafloor confirmed by 2D data. It suggests that fluid flow is guided by these faults.

Chaotic reflectors with high amplitudes are observed just above the Top Kai horizon and only on the GGV. These high amplitudes are observed both on 3D and 2D data.

On one line of the newly acquired 2D data, lenticular bodies are observed with a negative reflectivity at the top, which may indicate the presence of gas. In addition, another structure similar to GGV, but smaller was discovered. It shows the same character at all stratigraphic levels, which seems to indicate that the GGV has satellite structures with the same origin. The seismic coverage does not allow deciding whether this structure is isolated, or part of a cluster surrounding the GGV.

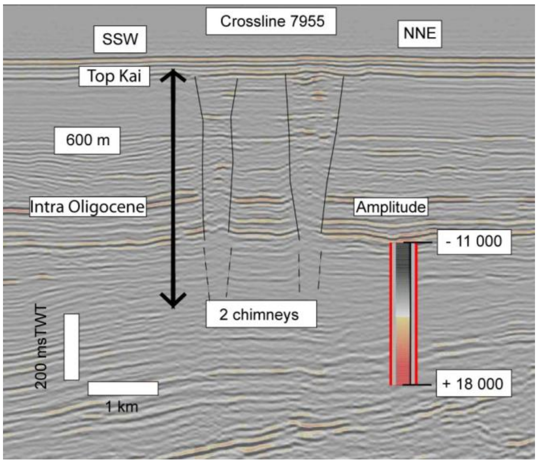

Figure 1: Crossline 7955 en amplitude

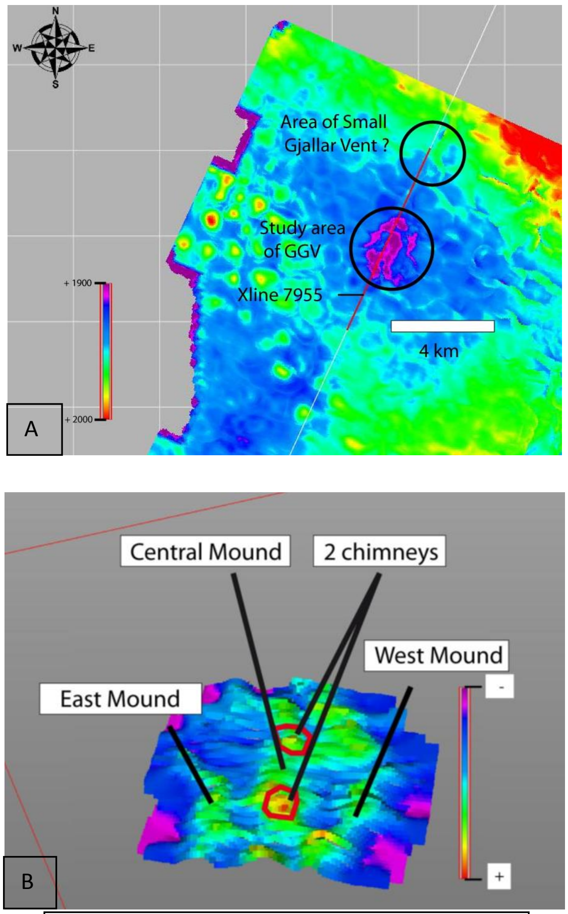

Figure 2: Base map of Top Kai horizon (A) and 3D view (B) (isochron).

A MODELLING APPROACH FOR A BETTER UNDERSTANDING OF FACTORS CONTROLING THE CARBON ISOTOPIC COMPOSITION OF AUTHIGENIC CARBONATES

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Hydrocarbon-rich fluids discharges at ocean margins are typically associated with authigenic carbonates. It is firmly recognized that their mineralization is mediated by a microbial consortium that oxidizes reduced hydrocarbons into dissolved inorganic carbon. This reaction, so called the anaerobic oxidation of methane (AOM) is fuelled by rising fluids transporting methane and by the sulphate incoming from bottom seawater. At the sulphate methane transition zone, alkalinity increases in the pore-water by the production of methane-derived bicarbonate lead to the precipitation of authigenic carbonates.

The carbon isotopic composition ($\delta^{13}C$) of authigenic carbonates is usually used to track the origin of carbon however it is still only partially understood what factors influence their signature. For example, it has been proposed that alternative microbially-mediated oxidation of short-chain hydrocarbons and organo-clastic sulphate reduction can contribute significantly to the increase of pore water alkalinity. Another consideration that has not been studied extensively is the fact that rising fluids can supply important amounts of dissolved inorganic carbon to the sulphate methane transition zone and thus, impact the carbon isotopic composition of carbonates.

The preliminary results provided by our transport-reaction model indicate that the origin and consequently the carbon isotopic composition of methane is coherently an important factor. The imprint of alkaline fluids enriched in ^{13}C can contribute to form moderately depleted authigenic carbonate (around -20‰ VPDB). Despite of their lower solubility and unfavourable stoichiometry, the oxidation of hydrocarbons heavier than methane (i.e. ethane) can form authigenic carbonate but only in case of high microbial turnover which are thought to be unrealistic.

ASSESSMENT OF THE SULFATE-METHANE TRANSITION ZONE (SMTZ) ALONG A LONGITUDINAL TRANSECT IN RÍA DE VIGO (NW SPAIN)

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In Ría de Vigo, the high biological productivity may lead to the deposition of organic-rich mud. Methane is formed in those sediments due to the microbial degradation of the organic matter. Shallow gas accumulations of methane are currently distributed all along the ría (Iglesias & García-Gil, 2004). The sediment horizon where methane and sulfate coexist, and where they are consumed during AOM (Borowski et al., 1999) is referred to as the SMTZ. This zone works as a methane barrier for the upward diffusing methane, and its thickness is determined by the organic carbon flux to the sediments.

The Ría de Vigo, in the northwest Iberian Peninsula, is a large submerged, incised valley which is orientated SW-NE. The water depth increases from 10 m in the San Simón Bay, to 50 m in the south mouth of the ría.

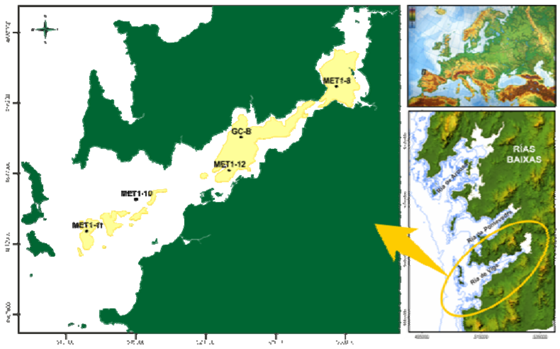

Fig.1. Geographical context of Ría de Vigo. It is shown the cores location and the mapped shallow gas fields.

In order to characterize the gas fields five gravity cores were extracted, four of them located inside the gas fields and the other (control) in an area without gas (Fig. 1). The core GC-B was extracted in May 2008 within a mussel raft polygon, while the others (MET1-8, MET1-12, MET1-10 and MET1-11) were recovered in June 2010. In each one, porewater SO_4^{-2}, CH_4 in sediments, TOC, TC, TN, pH, Eh, temperature and salinity were measured. Furthermore, facies analysis was performed.

Textural analysis showed that facies are fine-grained sediment (mud) with slight content of bioclastic sand. A little increase in the coarse (sand) fraction in the external cores was observed. Methane and sulphate profiles (Fig. 2) allowed distinguish a SMTZ in each core. A gradual increase of the SMTZ depth is observed toward the outer part of the ría, coinciding with an increase of the water depth. In cores MET1-8 and GC-B (retrieved at 10 m and 22.5 m water depth respectively) SMTZ is located around 60-100 cm, while in core MET1-11 (38 m water depth), SMTZ is identified between 210-230 cm. Excepting core GC-B, below the SMTZ still appear sulphate.

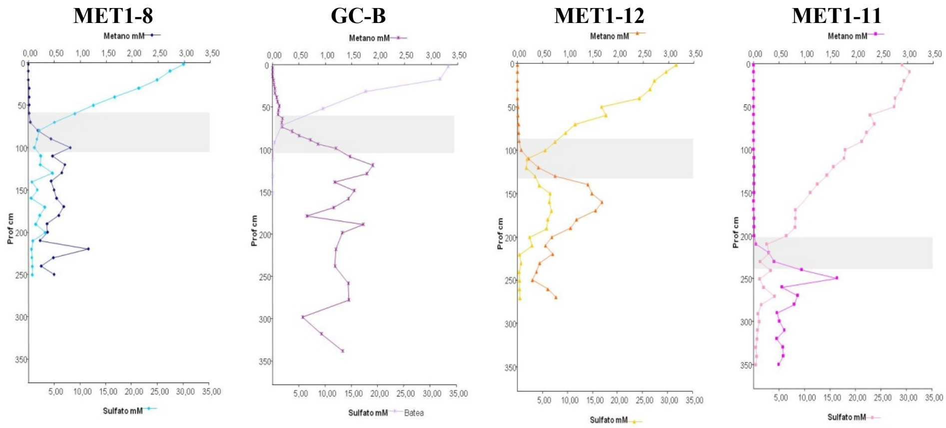

Fig. 2. Methane and sulphate profiles from cores.

It is also noticeable the variation in CH_4 concentrations among the different cores (Fig. 2). Cores GC-B (average 1.15 mM) and MET1-8 (average 0.52 mM) respectively evidence the highest and lowest methane concentration recorded. TOC analysis show great differences between cores placed in the outer-middle part of the ría (MET1-11, MET1-10, MET1-12 and GC-B) and the core located in San Simón Bay (MET1-8). Core MET1-8 has an average value of 7% TOC (ranging between 4.3 and 10.0 %) while the rest of the cores have values around 1.8-3.5 % TOC (1.2 to 3.4 %). In contrast, methane concentrations are lower in San Simón Bay (inner part of the ría) than in the rest. This fact can be due to the different composition of the organic matter with TOC/TN higher than 10 in San Simón Bay which are representative of organic matter from continental origin (Hedges et al., 1997). In the others cores, TOC/TN ratio is lower than 10 in the surface, representative of a more labile organic matter, of mainly marine origin.

Acknowledgements:
This work was funded by the Ministerio de Ciencia e Innovación (MICINN) under research projects CTM2009–13926-C02-01 and CTM2009-08158-E, and by Xunta de Galicia project 10MDS310020PR. N. Martínez-Carreño was funded by the FPI research Grant from MICINN. We would like to thank Seismic Micro-Technology Inc., who provided free Licences of Kingdom Suite software

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SEDIMENT GEOCHEMISTRY AND BENTHIC FORAMINIFERA DISTRIBUTION IN AN ACTIVE METHANE SEEP ENVIRONMENT, BAIA DE BERTODANO, SEYMOUR (MARAMBIO) ISLAND, ANTARTIC: PRELIMINARY RESULTS

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The collapse of a significant portion (12,500 km^2) of Larsen ice shelf, together with the increase of the atmospheric temperature in the western Antarctic that occurred during the last decades, reactivated the discussion about the stability of the ice cover in this region. It also raised the question of the impact of methane seeps on the benthos in cold waters.

It is reported in the literature that the rapid heating of the Weddell Sea would induce thermal dissociation of gas hydrate in the area of Admiralty Sound, between Seymour and Snow Hill islands. Studies carried out in the area revealed gas seeps (mostly methane) in shallow areas (<12m).

A sampling campaign was carried out around one of these seeps in March 2011. Thirty two stations were sampled in the Bertodano Bay, located between Boadman Point and Cape Wiman, Seymour Island. At each station, physic-chemical parameters were measured in surface, bottom, and intermediate waters. A Van-Veen grab sampler was used to collect superficial sediment samples for grain size analyses, geochemical analyses and determination of live benthic foraminifers.

For geochemical analyses (total organic carbon, total nitrogen and total sulfur), whole sediments were dried at 60°C and homogenized in an agata mill. The analyses were performed on a LECO® CNS 2000 analyzer. TOC/TN and TOC/OP ratios were calculated to determine the source and nature of organic matter in superficial sediments. Elemental TOC/TS ratios were calculated to determine a qualitative indication of the redox status of the sediments and overlaying water column.

Trace elements were investigated in aliquots of the whole homogenized reduced to a fine powder using agate mill and the concentrations were determined by ICP MS (Perkin Elmer Elan 9000).

The study area is shallow (0.5 to 6,90 m) and weakly stratified. Water temperature and salinity ranged from –0,42°C to –1.09°C and from 32.8 to 34.9, respectively. The pH is slightly alkaline (7.79 – 8.26). Values of Eh (39 – 293mV) and of dissolved oxygen (11.27 – 18.79 mg l^{-1}) indicate an oxic water column. Turbidity ranged from 0.1 to 40.6 NTU.

Sediments are mostly lithoclastic ($CaCO_3$ < 30%), sandy (very fine sand), with low concentrations of total organic carbon (0.13 – 0.72%), total nitrogen (0.01 – 0.09) and total sulphur (0.04 – 0.26%).

The values of C/S ratio (1,97 – 4.59) indicate a sediment deposition oxic and in hypoxic to anoxic conditions, under a water column mostly oxic, with periodic hypoxia. The values of C/N ratio (4.7 – 48) suggest organic matter predominantly of continental origin, secondarily mixed with organic matter of marine origin.

The highest concentrations of rare earth elements and yttrium (*e.g.*, Ce - 62ppm, La= 29ppm, Y – 11ppm) are found in the central part of the study area, particularly at station P10, located at a short distance from the coast.

Preliminary results show that the assemblages of stained (living) foraminifera are dominated by monothalamous species followed by agglutinated species. Calcareous specimens are rare. These assemblages have strong similarity with assemblages reported from neighboring area, located in the other side of Seymour Island, but are different from assemblages of temperate regions subjected to methane seep.

Projeto PROANTAR (557036-2009-7)

HIGH-RESOLUTION GEOPHYSICAL IMAGERY OF THE ACTIVE AMSTERDAM MUD VOLCANO (ANAXIMANDER MOUNTAINS, EASTERN MEDITERRANEAN)

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The Anaximander Mountains rise more than 2000 m above the seafloor at the junction of the Hellenic and Cyprus arcs in the eastern Mediterranean. These tectonic features are formed by the southward rifting of crustal blocks from southwest Turkey (Woodside et al., 1998). A number of active mud volcanoes are associated with the mountains, including the Amsterdam mud volcano (AMV), one of the largest mud volcanoes of the Mediterranean with a 3 km diameter. The location of AMV and its seepage activity are tectonically controlled (Zitter et al., 2005, 2006). AMV exhibits extensive and voluminous mud flows and collapse structures. It is characterized by long-lasting discharges of hydrocarbon-rich fluid emissions as indicated by the formation of authigenic carbonates. Shallow gas hydrates have been sampled at various locations (Zitter et al. 2005; Lykousis et al. 2009; Pape et al. 2010). The Amsterdam mud volcano was investigated with high-resolution seabed mapping tools, in 2004 (Mimes expedition, European Mediflux Program) with a deep towed side-scan sonar (IFM-Geomar EdgeTech, 75 kHz) and in 2007 (Medeco Leg1 expedition, EU FP6 Hermes Project) with a multibeam system (Reson 7125, 400 kHz) mounted on the Ifremer Victor6000 ROV. High-resolution bathymetry and backscatter data reveal the detailed morphology and seepage distribution at the AMV surface and several formation stages can be distinguished. Acoustic echoes were detected in the water column at its northwestern border and are interpreted as gas bubbles. A multiscale geophysical analysis of AMV is presented here with the emphasis given to its formation history and seepage activity.

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DOES SIZE MATTER? ON THE IMPORTANCE OF GRAIN SIZE IN THE MORPHOLOGY OF POCKMARKS FROM THE ATHENA SITE (CENTRAL NORTH SEA)

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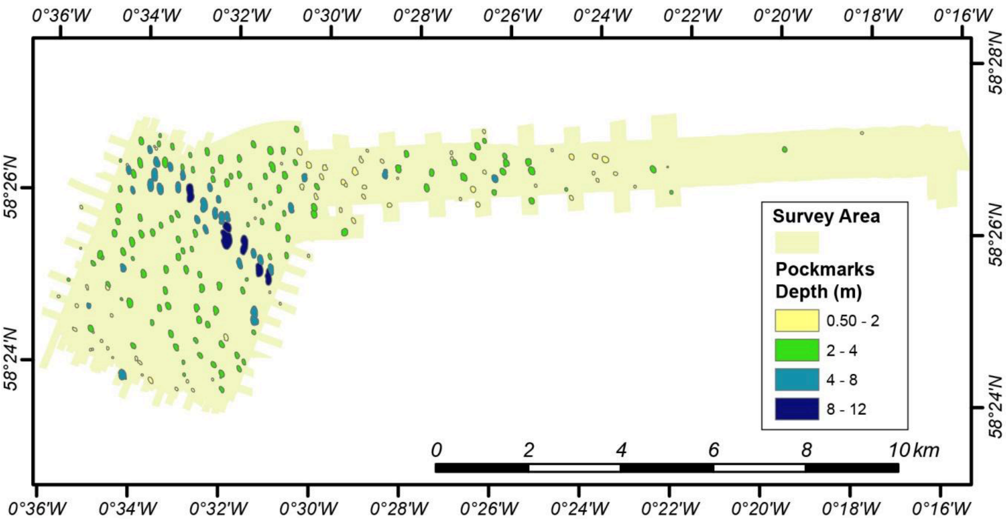
A semi-automated method of mapping and characterisation of pockmarks was used to identify and described morphologically the 225 pockmarks found within a 5 metres resolution bathymetric Survey from the Ithaca's Athena development, situated in block 14/18b in the Outer Moray Firth area of the UKCS on the western edge of the Witch Ground Basin. With a pockmark density of 5.03 pockmarks per square kilometre, almost 6% of the study area's seabed is shaped by pockmarks. The pockmark distribution is not uniform across the study area and their density decrease eastwards, being absent in the extreme east of the survey area where the late glacial/post glacial Witch Ground Formation deposits are virtually absent. Additionally, the general morphology of the pockmarks also varies spatially. The deepest pockmarks were found within or in close proximity of a gentle NW-SE depression present within the study area. The depth of these pockmarks can reach almost 12 m deep, well above the study area average of 3.02 meters deep. The 10 deepest pockmarks, all deeper than 7 metres, are aligned along the centre of that NW-SE depression. It's also along this depression that the largest pockmarks are found, with areas greater than 2000 km^2.

It often stated that the grain size of seabed sediments is a controlling factor in the size of pockmarks and explains why pockmarks are not reported in sandy areas. However a recent examination of a suite of pockmarks on the edge of the Witch Ground Basin suggests that grain size may not be the controlling factor in pockmark size in at least this one instance. There are small changes in particle size analysis (PSA) of surface sediments but probably very minor compared with changes in pockmark size across the area. The range in sizes in this one small area is as great as seen across the whole Witch Ground Basin where there is a much greater variation in seabed sediment PSA. The variation in soft sediment thickness at Athena also varies as much as across whole of the Witch Ground Basin.



FLUID DYNAMICS AND SEISMISITY OF THE CASPIAN SEA

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Rhythms in hydrocarbon gassing are most obviously manifested in the periodicity of eruptions and activity of mud volcanoes that are accompanied by the release of hundreds of millions of cubic meters of methane, oil, and groundwater. The periodicity in eruptions established for a sufficiently long time interval indicates a stable dependence of mud volcanism on solar activity, fluctuations of the Caspian Sea level, and seismicity.

Activation of mud volcanism and seismicity in the region corresponds to phases of the Caspian Sea level falls. At the same time, measurements in geodetic test areas and GPS measurements show almost meridional waves of rise and subsidence of block structures in the Caspian region that were responsible for alternating periods of compression and tension in the Caspian Sea depression. The extension phases correspond to sea-level falls. It is remarkable that the rhythms in these vertical movements correlate with phases of seismic and mud volcanism activity, variations in oil and gas production, and sea-level fluctuations.

The study of recent fluid dynamics in the Caspian Sea mud volcanoes provides an insight into the nature of past unique geological phenomena, e.g., absence of marine macro fauna and scarcity of micro fauna in the Early Pliocene basin. Based on drilling, seismoacoustic, and deep seismic profiling data, the mud volcanism in the South Caspian Basin commenced in the Early Miocene and became most intense at the Miocene-Pliocene boundary. This was accompanied by a dramatic sea level drop by more than 600 m (locally, up to 1500 m) in the Early Pliocene due to the paleo-Caspian sea isolation from the Eastern Paratethys as a result of the intense collision of the Arabian and Eurasian plates and the consequent rise of orogens surrounding the basin. Grandiosity of mud volcanism and fluid dynamics in the Caspian region is confirmed by paleogeologic reconstructions, geochemical studies, and basin modeling. Accordingly to these data, at the end of Miocene-Early Pliocene the Jurassic-Cretaceous rocks were involved into active fluid generation. This sedimentary complex is characterized by a higher gas-generation potential than the Paleogene-Miocene deposits that are source of recent volcanoes. The avalanche sedimentation rate reached 3.0-3.5 km/106 yr (occasionally, >4 km/106 yr) in the Early Pliocene basin. This indicates to extremely high subsidence rates, which are undoubtedly possible under conditions of intense fault tectonics. These faults were responsible for the mud volcanic fluid dynamics and redistribution of material within the sedimentary cover of the South Caspian Basin. They also served as conduits for abyssal fluids. This is evident from the detection of large buried (apparently root-free) columns (3-4 to 10 km across and 8-10 to 20 km high) in seismic time-sections. They penetrate the entire sedimentary cover up to the crystalline basement and are confined to contact zones of deep-seated faults that divide the South Caspian Basin into large blocks. The inflow of abyssal fluids to the Early Pliocene basin should undoubtedly have accompanied the subduction of the South Caspian oceanic crust under the

Middle Caspian continental plate that commenced 5.5 Ma ago (at the Pontian-Pliocene boundary).

At the beginning of the Early Pliocene, the dimension and volume of the paleo-Caspian basin reduced by several tens of times down to those of the present-day South Caspian Basin. At the same time, mud volcanism and abyssal fluid dynamics became more active, particularly in the central part of the basin, resulting in over saturation and intoxication of the desalinated basin by methane and the consequent mass extinction mollusks, fishes and other group of sea inhabitants.. This situation is probably responsible for the absence of macrofossils in the 6-7km thick Lower Pliocene sequence that accumulated over 2.0-2.5 Ma.

Special place for fluid dynamics and environment of Caspian Sea and surrounding area have gas hydrates associated with submarine volcanism. The large accumulations of gas hydrates are confined to bottom sediments of the Caspian Sea deposited in mud volcanoes craters (interval of sediments 0-0.4 m, sea depth 480 m) and volcanoes bodies.

Caspian Sea being the closed basin is very sensitive to climatic and tectonic events expressed in the sea level fluctuations. In regressive stages as a result of sea level fall and reducing of hydrostatic pressure the decomposition of gas hydrates and releasing of great volume of HC gases consist mainly of methane are observed. Paleoreconstructions show that good conditions for large gas hydrate formation and accumulations existed in South Caspian basin in late Miocene (Pontian). Consequently, dramatic sea level fall in Lower Pliocene could provoke destabilization of gas hydrates and massive release of hydrocarbon gases to water column that led to strong intoxication of marine water. In other case massive dissociation of gas hydrates could liberate enough methane in atmosphere to cause serious climatic perturbations.

In Upper Pliocene and Quaternary mud volcanism occurred under the conditions of semi-closed basin periodically connected with Black and Mediterranean Seas. The increase of water surface and differently oriented currents stimulated rapid mixing of gas-saturated waters and reduction of background concentrations of hydrocarbon gases. The same picture is observed in the modern Caspian Sea. Such stages of the Caspian Sea history are characterized by the revival of Caspian organic world.

South Caspian sedimentary basin is an unique area with thick Mesozoic-Cenozoic sediments (up to 30-32 km) characterized by an extremely high fluid generation potential. A great amount of active mud volcanoes and volume of their gas emissions prove the vast scale of fluid generation.

The data received show the close relation of mud volcanic fluid dynamics in the South Caspian basin with sea level change and seismicity which provide enormous influence on Caspian Sea environment in geological past and present days.

CHARACTERISTICS OF HYDRATE-BOUND GAS AND DISSOLVED GAS IN PORE WATER OFF SAKHALIN ISLAND, SEA OF OKHOTSK

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Natural gas hydrates are considered to be a possible global source of energy and are also of concern as a large reservoir of methane, which may cause global warming by dissociation. Near-surface gas hydrates exist in the seepage sites of off Sakhalin Island, the Sea of Okhotsk, where gas plumes are ascending from the sea floor. They contain not only methane but also small amounts of other higher hydrocarbons (ethane, propane, etc.), CO_2, and H_2S. More than ten gas seep sites have been discovered since 1990s in the north area of the Lavrentyev seabed fault (NE Sakhalin Island) and hydrate-bearing sediments were recovered by using a gravity corer. Recently, Sakhalin Slope Gas Hydrate (SSGH) project was started in 2007 and hydrate-bearing sediment cores have been retrieved from the southern area of the Lavrentyev Fault in 2009-2011. We obtained the samples of hydrate-bound gas and dissolved gas in pore water on board, and we investigated molecular and stable isotope compositions of them. Empirical classification of the methane stable isotopes; $\delta^{13}C$ and δD indicated their microbial origin via carbonate reduction. Profiles of methane concentration in the pore water suggested a shallow SMI (sulfate-methane interface) and high methane flux from the deep sediment layer. SMI depth was estimated as 30-50cm from the sea floor in the case of hydrate-bearing cores, and around 2m from the sea floor in the case of gas-rich cores. Molecular compositions of hydrate-bound gas were almost the same in both northern and southern areas of Lavrentyev Fault. Stable isotope compositions of hydrate-bound methane were concentrated in the range of -204.6‰ to -196.7‰ for δD and -66.0‰ to -63.2‰ for $\delta^{13}C$ in the north area, whereas both isotopes were more depleted in the south area about 6‰ in ^{13}C and 7‰ in deuterium, respectively, suggested much more active microbial processes in the shallow sediment. δ13C of hydrate-bound ethane was also depleted (-53‰ to -40‰) in the south area, whereas that in the north area distributed in the range of -41‰ to -27‰. We conclude that the origin of hydrate-bound gas is mainly microbial in the south area and small amount of thermogenic gas mixes with microbial gas in the north area of the Lavrentyev Fault. We also found an isotopic difference in methane δD caused by the process of isotopic fractionation in the hydrate sample retrieved from the south area, and Raman spectroscopic analysis revealed that hydrogen sulfide molecules are also encaged in the hydrate crystals, and we found heterogeneous molecular composition of hydrate-bound gas in the hydrate samples. A ratio of cage occupancies of H_2S molecules between large and small cages revealed that H_2S molecules are rather encaged in the small cages in contrast to methane molecules.

Seep carbonates: seismic expression vs. outcrop observations

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In this study we compare the expression of seep carbonates as high-amplitude patches on seismic data with the ground truth of outcrop analogues. The organizations of two different outcrops of methanogenic carbonates were compared with the positive high amplitude anomalies (PHAAs) that we observed in a high resolution 3-D seismic survey in Offshore Angola.

On seismic records, patches of positive high-amplitude anomalies commonly occur in the middle of hemipelagic series in continental slope settings. Individual PHAAs are typically sub-circular or elongate, and stack up vertically over several hundred meters in some cases. PHAAs associated with acoustic chimneys or pockmarks, have been studied on a 3-D seismic survey of Offshore Angola. They correspond to seismically fast and high-impedance material, and often generate seismic pull-up effects. In the context of soft background, deep-sea sediments, such in our 3-D seismic survey, PHAAs are interpreted as methanogenic carbonates.

Two outcrops of methanogenic carbonates in NW Spain (Mutriku, Kardala outcrop) and in SE France (Gigors) indicate that the lithologies that compose the methanogenic carbonates are rather heterogeneous:

- The Kardala carbonate lens (over 30-m long and 5-m thick) reported by Agirrezabala (2009) in Mutriku is located above a fault, and is comparable with the smallest elongate PHAA seen on our survey, both as regards the size and the location above a fault (Fig. 1). The Kardala lens is composed by the aggregation of: oil-stained or bitumen-filled methanogenic carbonate nodules/conduits, either isolated or clustered, carbonate cements and benthic macrofossils.
- The vertical succession (over 80 m) of well continuous methanogenic carbonate layers in Gigors (Fig. 2) also shows heterogeneity both horizontally and vertically (see also Blouet et al., this volume). The carbonate layers are not pure but contain shale or coarse grained sands, macro and microfossils. Their individual thickness is less than seismic resolution, which means that seismic would respond in this configuration primarily to the stacking pattern of the beds. The soft / hard alternations could be similar to stacked anomalies observed offshore Angola.

Our outcrop observations point out that within the limit of typical seismic resolution, the lithology of methanogenic carbonate is commonly heterogeneous. Variation in the lithology of both the carbonates and encasing shales (presence of silt / sand / shale) in the carbonates and variable carbonate content of the marls will further affect the response by modifying acoustic impedance.

All of these inspire that, impedances of PHAAs vary in seismic data, depend on the vertical organization of the hard (carbonates) layers and their vertical spacing, but also lithological characters and heterogeneous compositions of the hard (carbonates) layers.

Forward seismic modeling in progress will provide additional insight in the actual effect of heterogeneity in the bedding, and may help interpreting the actual lithology behind our seismic records, at least the variability that may be involved.

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Blouet, J. P., Imbert, P., Ho, S., this volume. Morphology variations of methanogenic carbonates in relationship with their genesis mechanisms, Vocontian Basin, France: a multidisciplinary study.

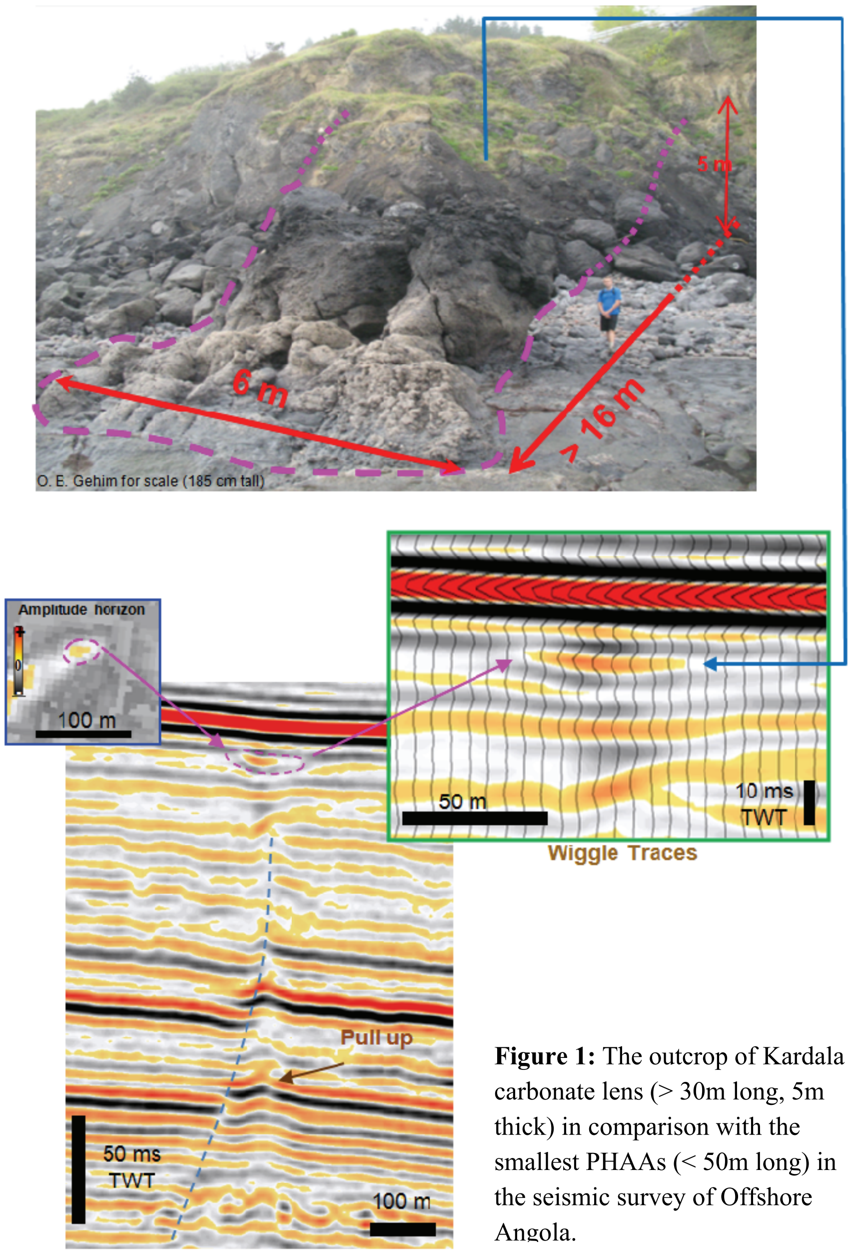

Figure 1: The outcrop of Kardala carbonate lens (> 30m long, 5m thick) in comparison with the smallest PHAAs (< 50m long) in the seismic survey of Offshore Angola.

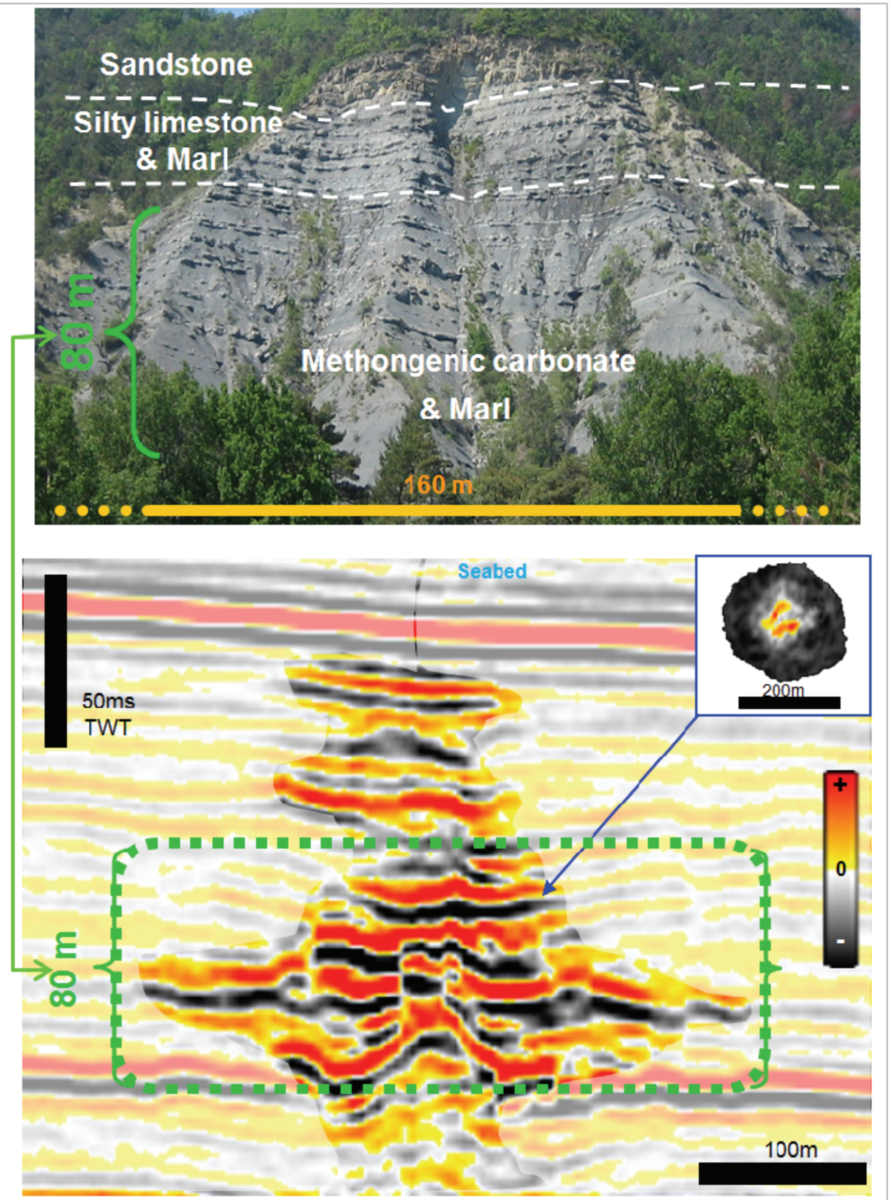

Figure 2: The outcrop of a vertical succession in Gigors (~ 80m) in comparison with the stacked PHAAs in the seismic survey of Offshore

Anaerobic methane oxidation and its influences on the sulfate reduction and sulfur isotopic compositions

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Biogeochemical sulfur cyclein methane dominated environmentinvolved complex microbial andmigration processes. Sulfur isotopic fractionations in such environment could provide valuable information to resolvedegree of microbial mediate biogeochemical processes and physical advection and diffusion migration occurring in sediment. In order to evaluate extent of anaerobic methane oxidation and its influence on sulfur isotopic fractionation in the study environment, anumerical 1-D transport-reaction model including sulfate reduction, anaerobic methane oxidationand isotopic fractionation were applied to the observed variations in concentrations of sulfur species (pore water sulfate, dissolved sulfide, pyrite) and isotopic $\delta^{34}S$.

Study sediments were taken on *r/v Marion Dufrensene,* cruise 178 using a Calypso giant piston core in the Yung-An Ridge, offshore southwestern Taiwan.Across the Ridge, depth of sulfate-methane transition zone(SMTZ) varied accordingly, with methane concentrations increased with increasing depth. Similarly,pyriteconcentrations and spatial and vertical sulfur isotopic variations were also found in study area sediments. Depth of the SMTZranged between 1 m to 8 m, with maximum dissolved sulfide reaching8mM. Pore water sulfate $\delta^{34}S$ values range from +20.5‰ to +52.9‰ with an initial seawater value of 20.3‰ at the sediment water interface. Based on Rayleigh fractionation calculation, sulfur isotopic fractionation factors were in range between 1.008 to 1.014. However, $\delta^{34}S$ values of pyrite ranged widely,from -19.7‰ to +9.9‰. High pyrite-S contents were found together with heavier pyrite-S isotopic composition while lower pyrite-S concentrations always associated with negative and lighter pyrite-S isotopic signature. Typically,pyrite-S isotopic compositions found in normal marine sediments showed negative values.In our study sites, pyrite isotopic compositionsof sediments near the SMTZ were characterized with positive and heavier $\delta^{34}S$.

EXPERIMENTAL RESULTS FOR ENHANCED RECOVERY OF METHANE HYDRATE USING EXOTHERMIC HEAT OF CO_2 HYDRATE

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Methane hydrate is expected as natural gas resources in the future. On the other hand, there would be a subject for commercial production. Then some researches are carried out for enhanced recovery of methane hydrate. Our institute had proposed a heating method using exothermic heat of CO_2 hydrate formation. A CO_2 injection technique for the heating is experimentally tested. We had also proposed a new injection technique using CO_2/water emulsion in order to control phase change from liquid to solid. We had obtained data with high reproducibility that show a heating at the front of emulsion flow, the heating position is moved with the seepage of the emulsion though saturated super cooled Toyoura sand in a pressure cell. And the emulsion would flow through sedimentary layers that are warmed to the phase equilibrium condition by the exothermic heat. CO_2 could not be conventionally injected to the saturated layers that temperature is less than or equal to 10 degree Celsius, because the formed solid CO_2 hydrate blocks the pore of the sediments. The emulsion could improve the blocking phenomena, then CO_2 hydrate can be formed a few ten percent of the pore, and the remained pore can be used for emulsion flow. If this warming flow of CO_2 emulsion works in the field stratum, CO_2 could be injected for long term.

COLLAPSED FUNNELS OFFSHORE AUSTRALIA: EVIDENCE FOR PAST HYDRATE POCKMARKS?

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Three-dimensional seismic data from the Carnarvon Basin (deep offshore Australia, NW shelf area) show three to five erosional surfaces over an area covering several thousands of km². Mapping of these surfaces shows that the erosional surfaces are made up of coalescing craters, roughly circular to very elongate, with a depth of several hundred meters and diameters reaching several kilometers. The overall aspect of the surface reminds of classical stylolites in carbonates, but about 10^5 to 10^6 times bigger.

Detailed seismic picking inside some of the craters show that the seismic character of their infill matches that of the outside. The most likely interpretation is that the craters are collapse features, from which rock volumes on the order of 1 km^3 was removed under sedimentary cover.

Several hypotheses were tested to account for that removal of sediment under cover, for instance karstification, or involving gas hydrates, but all seemed a bit far-fetched in the absence of a suitable analogue.

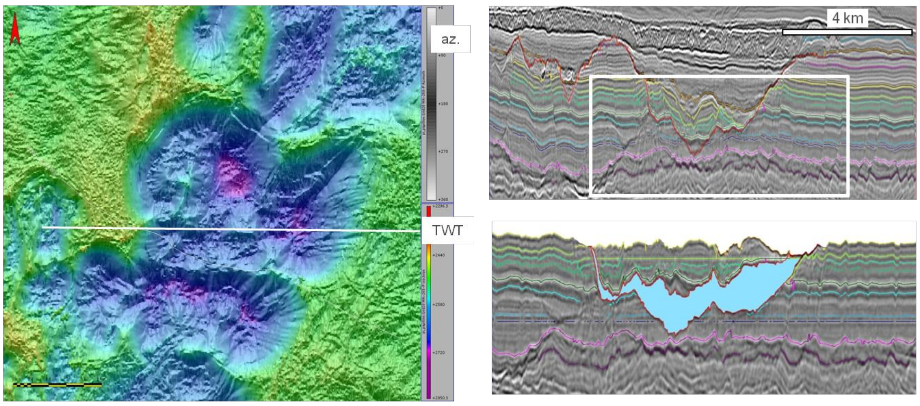

Fig.1: one cluster of collapsed funnels from the NW shelf of Australia. Map view, Two-way time with dip azimuth in overlay. Section views along the white line on the map. Bottom line is graphically restored by simultaneous flattening on a horizon below the funnel and one above

While this example was being worked out, high-resolution seismic was acquired and calibrated by CPT (cone penetration tool) and shallow coring offshore Nigeria. Part of the acquisition was focused on irregular pockmarks that turned out to be hydrate-bearing, some of them with a deep plug of methane hydrates forming a V-shaped cone below the pockmark. One similar irregular pockmark with low relief (Fig. 2) is interpreted to reflect progressive demise of hydrates from the base of the pockmark, causing progressive foundering of the infill down into the cone (Sultan et al., 2010).

Put together, these observations suggest that the collapsed funnels of Australia are probably fossil hydrate pockmarks that collapsed as the hydrate stability field rose up due to ongoing sedimentation. It is interesting to note that two of the three episodes of dissociation occurred in close temporal vicinity to the Paleocene and Eocene hyperthermals, suggesting a possible causal relationship.

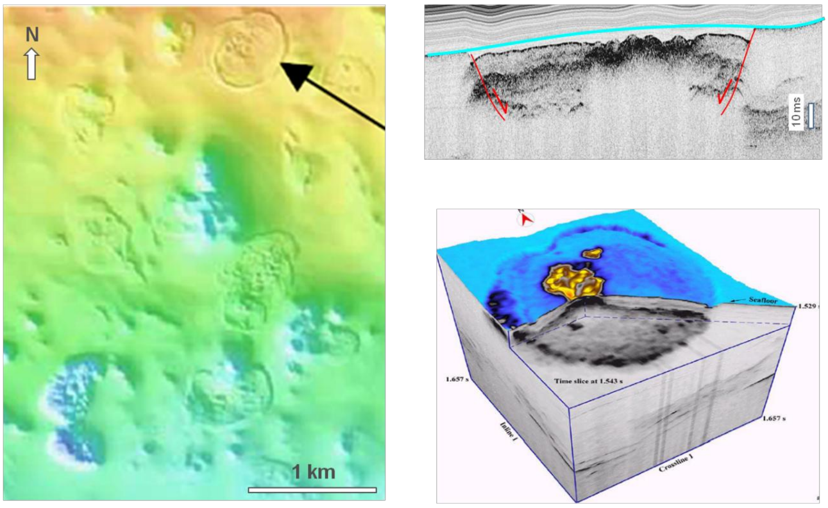

Fig. 2: cluster of irregular pockmarks. The seismic line on the right is a N-S cross-section of the arrowed pockmark; the cyan line interpolates the seafloor between the edges of the pockmarks and shows a slight depression. The way the seafloor abuts onto the edge suggests active normal faulting. The block diagram on the bottom shows the reflectivity of the seafloor (yellow = high to cyan = low); sampling has shown the presence of hydrate in the reflective patch in the middle.

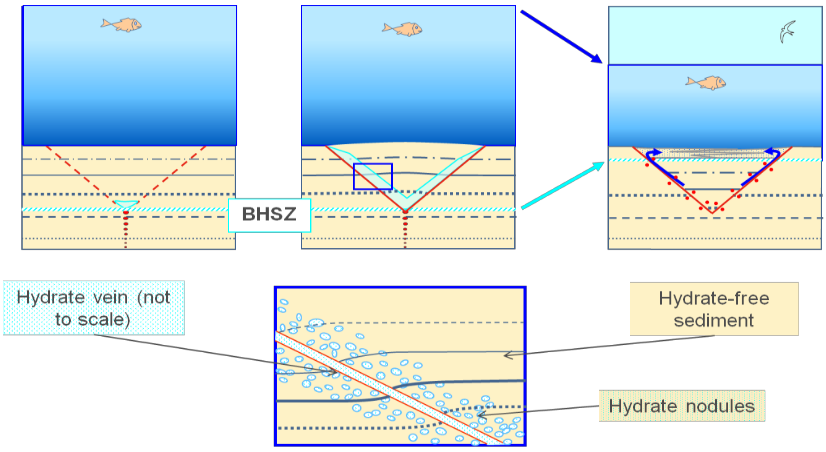

Fig. 3: interpreted process of formation of the collapsed pockmarks of Australia. Hydrate-bearing sediment (close-up on lower image) is interpreted to be expelled along with the hydrates themselves upon their dissociation / dissolution. The reason of hydrate dissolution / dissociation is depicted here as a relative sea-level fall, but it may also be a consequence of the Paleocene / Eocene hyperthermals

AREA CLASSIFICATION OF NEAR-SURFACE ACCUMULATIONS OF GAS HYDRATES IN BOTTOM SEDIMENTS OF LAKE BAIKAL

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Significant accumulations of oil and gas are concentrated in the bottom sediments of Lake Baikal. Some of the gas accumulations in the form of gas hydrates have been found both at a depth of up to 400 m below the lake floor and near its surface. From 2010 to 2011, the data obtained by using a multibeam echosounder, from the MIR submersibles, and from the processing of the previous geophysical results have allowed us to discover 11 new sites of near-surface gas-hydrate accumulations in addition to the ten previously known accumulations. As before, most of the sites are associated with mud volcanoes and some with gas discharge; however, we have also found accumulations with no obvious lake-floor topography or gas discharge. For instance, we observed such accumulations on the slope of underwater high Posolskaya Bank in South Basin of the lake, where gas hydrates of structure II have been discovered for the first time. Such type of gas hydrate structure has previously only been found in the Central Basin, near the Kukuy Canyon.

So far, 21 sites of gas hydrate occurrence have been discovered. Gas hydrates are of structure I and II, which are of thermogenic, microbial, and mixed origin. At 15 of these sites, gas hydrates were found in mud volcanoes, the remaining six near gas discharges. Additionally, depending on the type of discharge and gas hydrate structure, the gas hydrate occurrences were visually different. Therefore, it is possible to classify gas hydrate accumulations in Lake Baikal according to the type of gas present in the hydrates and to identify the sites on the lake floor along fault zones which allow thermogenic ethane from sufficiently great depths to go through the lower boundary of gas hydrate stability zone and form mixed type of gas.

This work was supported by the International Science and Technology Center (ISTC Project #4016), the Presidium of the Russian Academy of Sciences (Project №21.8 under the program of basic research of the Presidium of the Russian Academy of Sciences), FWO (Fonds Wetenschappelijk Onderzoek) Flanders project 1.5.198.09., Grant-in-Aid for Scientific Research 19550077, 21254006, 21360219, 22540485, and 23254008 by Japan Society for the Promotion of Science, and Fund for Protection of Lake Baikal.

FIRST ATTEMPTS TO MAP THE TOP OF GAS HYDRATE ACCUMULATIONS IN BOTTOM SEDIMENTS OF LAKE BAIKAL

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Lake Baikal is the world's unique freshwater reservoir, which bottom sediments were found to contain subsurface and near-surface gas hydrate accumulations. Investigations of their distribution were carried out at certain points. To attempt areal mapping of the top of gas hydrate accumulations, we have chosen the gas seep site, Goloustnoe where some temporal and constant gas seepages were earlier found. Near the seepages, first meters of bottom sediments were observed to have gas hydrate layers, which discharges were also found using deep-sea manned submersibles MIR. In addition, we have earlier performed experiment on extraction of gas from gas hydrates by their in situ dissolution. We have mapped the site area of 500 m^2 by using the tip resistance measured by a cone penetration test. The report deals with mapping methods and, as a result, the map of occurrence depth of gas hydrate top layer. We also discuss regularities in occurrence depth and distribution of gas hydrates depending on source of gas discharge in the form of bubbles and bottom topography.

This work was supported by the International Science and Technology Center (ISTC Project #4016), the Presidium of the Russian Academy of Sciences (Project №21.8 under the program of basic research of the Presidium of the Russian Academy of Sciences), and the Siberian Branch of the Russian Academy of Sciences (Project № VII. 65.2.5 under the SB RASf undamental research program).

Gas Fluxes through chemosynthetic ecosystem living in three areas of the gulf of Guinea (Equatorial Atlantic ocean).

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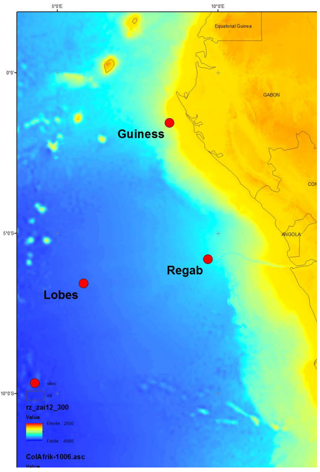
Cold -seep areas on continental margins are characterised by biogeochemical processes that leads to the development of chemosynthetic ecosystems on the seabed and to the precipitation of authigenous minerals. These processes associated with the migration of methane-rich fluids depend on microbial activity in the sediments. The anaerobic oxidation of methane coupled with the reduction of sulfate allows formation of carbonates and generates high concentrations of interstitial hydrogen sulphide. Both hard substrata and reduced compounds (sulphides and methane) allow the development of rich and diverse communities. The communities of the cold fluids have a strong spatial structuring related to the heterogeneity of the environment.



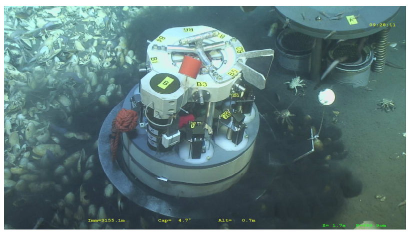
During the WACS cruise (January-February 2011) in the Gulf of Guinea on the *N.O. Pourquoi pas?*, measurements of gas fluxes at the water/sediments interface were obtained using the benthic chamber (CALMAR) deployed with the ROV *Victor* at three different areas.

The first zone, called Regab, is a giant pockmark of 800 m diameter, at 3200 m depth, along the Congo margin. It is characterized by a high habitat heterogeneity, with assemblages of the three major symbiont-bearing taxa encountered at cold seeps: Vesicomyidae and Mytilidae bivalves and Siboglinidae polychaetes, as well as microbial mats.

The second zone called Guiness gathered several small, less active pockmarks located in the Gabon margin, about 500 km north-west of Regab, at 700 m depth.

The third zone is located in the distal lobe complex of the Congo deep-sea fan, at 5000 m depth, and is characterized by huge organic inputs from the Congo canyon/channel system and the presence of biological communities which resembles those observed on pockmarks.

Five benthic chambers (CALMAR) were deployed, on Bivalve *Vesicomyides* habitats : two at Regab, one at Guiness and two at Lobe stations area. The combined measurement of oxygen, sulphides, methane, total CO2 and ammonia is used to estimate the fluxes of the different compounds.



The benthic chamber Calmar during the incubation by 3200 m depth

The first observation is the very high oxygen consumption (172- 434 mmoles m^{-2} d^{-1}) under the benthic chambers and conversely, a high production of CO_2 (37- 1857 mmoles m^{-2} d^{-1}). The consequence of this is a strong variation of the respiratory coefficient from 0.8 to 5.2. These results can be explained essentially by the biological respiration of the bivalves and secondarily by the dissolution of the carbonate to explain the CO_2 flux. The positive flux of ammonia (2.9- 71.8 μmoles m^{-2} d^{-1}) is associated to the nitrogen excretion produced by the bivalve metabolism. The cold seep ecosystem is connected to the production of methane which varied to 1.8–139 mmoles m^{-2} d^{-1} and sulphide flux was observed only at the shallower station (156 mmoles m^{-2} d^{-1}).

MULTISCALE STUDY OF SEEP STRUCTURES – OPOUAWE BANK, OFFSHORE NEW ZEALAND

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We present a multi-scale geophysical study of several methane seep sites located on Opouawe Bank, an accretionary ridge at the southern Hikurangi Margin offshore New Zealand's North Island. Multichannel seismic (3D P-Cable), parametric echosounder (Parasound), deep-towed sidescan sonar and subbottom profiler data were combined to image the spatial structure of the seeps and their expression at the seafloor.

The data were acquired in March 2011 during cruise SO214 with the German R/V SONNE. The aim of the project was to investigate cold seep structures within the gas hydrate stability zone (GHSZ). 3D P-Cable seismic reflection data reveal the sub-seafloor structure of gas migration pathways beneath six seep sites, which can be traced to a source that is at least as deep as the base of the GHSZ. Bottom simulating reflectors are visible, but interrupted underneath the active seep sites. The feeder channels of the seeps seem to be elongated perpendicular to the strike of the ridge. Some of these conduits show internal reflections. The number of feeder channels varies for the different seep sites, though some of them seem to be stalled.

Multiple Parasound transects were acquired concurrently with the 3D P-Cable survey. They reveal the shallow structure of the upper 50 m - 100 m of the gas conduits in very high detail. Pronounced, sub-vertical, low-amplitude zones are observed throughout the dataset beneath the known seep sites. Additionally, however, numerous sub-vertical zones of suppressed reflectivity are observed in other areas. Many of the zones do not reach the seafloor, terminating at various stratigraphic levels. Strong reflections are often observed within the low-amplitude zone close to the seafloor, which are likely to be caused by the presence of gas. The high-frequency component of the Parasound system was used to image numerous flares in the water column, revealing that gas is actively venting from the seafloor at the sites.

Sidescan sonar data reveal different types of backscatter behavior, which reflects the amount of carbonate precipitated on the seafloor. One seep site called Takahe is marked by slightly elevated backscatter over a 0.059 km² large, oval-shaped area. Here, authigenic carbonates are not present on the seafloor, which distinguishes Takahe from the majority of the seeps on Opouawe Bank. Takahe is possibly a relatively young seep that has not been active long enough to precipitate carbonates onto the seafloor. The elevated backscatter may result from shallow gas accumulations, which is supported by acoustic turbidity in subbottom profiler data indicating the presence of gas only a few meters beneath the seafloor.

MORPHO-STRUCTURAL FEATURES OF EPISODIC MUD VOLCANISM IN THE GULF OF CÁDIZ.

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A morpho-structural analysis of several mud volcanoes (MVs) on the Moroccan Atlantic margin (Gulf of Cádiz) is presented. Multibeam data (bathymetry and backscatter), very high resolution seismic profiles from ultra-high resolution topographic parametric sounder (TOPAS) and gravity core data have been used. In all studied MVs have been recovered mud breccia overlain by a centimetric layer of hemipelagic sediments. Majority of MVs on the Western Morroccan Field display an asymmetric cone with flanks of different lengths. Asymmetric edifices are built on the slope of diapiric crests and their mud extrusions flow along one preferential direction from the emission centre. These MVs often have terraced profiles and several mud-flow events can be distinguished morphologically on their undulated surfaces with different backscatter values. At least four terraces have been observed along the flanks of certain MVs that are related to episodes of mud flows. The outflows form concentric, semi-circular structures of different backscatter which correlate with distinct smooth hyperbolic diffraction patterns on TOPAS seismic profiles. Evidence of these superimposed mudflow events has been detected in the gravity core MVSEIS-TG-11 recovered on Madrid MV where two layers of mud breccia have been detected interstratified between hemipelagic sediments. Mud volcanoes such as Madrid and El Cid have at least two stacked layers of mud breccia extrusions each one 0.5 m thick, intercalated between hemipelagic layers.

Depressions commonly occur in two main parts of such edifices: at the top and at the periphery. Both types of depressions are related to a mass defect below the edifice and/or relaxation of the compressional stress field due to the expulsion of sediment and fluids from the mud chamber. Patches of high and very high backscatter values have been detected inside the calderas (placed on their flat-topped summits) and in the rimmed collapsed depressions. This high and very high backscatter could be related to sites of focused fluid flow and the occurrence of HDAC precipitates.

The morphological features shown above allow defining geological processes and provide information about the nature and dynamics of mud extrusions. Mud volcanism is inherently episodic, with long periods of dormancy separating eruptions. The presented analysis reveals an episodic mud extrusion dynamic evidenced by the presence: (1) levels of mud breccia interbedded between hemipelagic layers, (2) lobated and terraced profiles with different backscatter values, (3) crater-like depressions and/or internal domes with patches of very high backscatter values. This episodic dynamic is framed in an evolutionary model constituted by periods of high activity of mud extrusions separated by quiescence ones. Depending on the tectonic setting and oceanographic conditions, a wide possibility of sedimentological and geomorphological features can take place in quiescent periods. Latent periods are located between active and quiescence ones, and are characterized by occurrence of gravitational collapses, landsliding and the precipitation of authigenic carbonates and polimetalic nodules and crusts.

Key words: Mud volcanoes, fluid flow, Gulf of Cádiz.

ACKNOWLEDGEMENTS

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VARIATION IN POCKMARKS IN COASTAL SETTINGS WEST OF SCOTLAND

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The Sea of Hebrides is an area of complex bathymetry on the UK continental shelf, west of the Scottish mainland. Its topography reflects extensive glacial erosion and proglacial glacial deposition in multiple basins ranging from fjordic environments – "sealochs", to inter-island troughs some of which extend 100s metres below sealevel. Seismic profiles have shown the presence of gas within the late glacial sediments which have been deposited very rapidly. In recent years a range of multibeam surveys have been conducted in this area by both national surveying agencies and academic groups. These surveys have shown that pockmarks are a common feature in a variety of settings.

An extensive area (2200 km^2) around the island of Rhum and Eigg (Fig 1) showed pockmarks often occur along linear trends, within seabed furrows, and are coincident with blanking of the pinger data. Generally the pockmarks occur where the underlying sediment is thickest in broadly linear deeps. These deeps are controlled by the predominantly ~north-south trending pre-Quaternary structures as well the buried glacial trough features. This relationship is most noticeable in Loch Slapin; offshore southern Skye where a near continuous (12 km) line of pockmarks delineates the axis of the deep. The largest pockmarks, exceeding 100m diameter and more than 10m deep occur over an area of 70 km^2, notably between Eigg and Arisaig.

Another survey off of Lewis shows pockmarks occuring in two lineations at right angles to each other. These pockmarks also display eccentricity reflecting the local hydrographic regime whose currents parallels one of the lineations. However some basins with thick accumulations of sediment in the Canna Basin where gas blanking is ubiquitous appear devoid of pockmarks. This suggests that there are additional controls on the development of pockmarks. Pockmarks are also found within several sealochs (Loch Broom, Loch Eribol and Loch Linnhe) often associated with extensive gas blanking with late glacial to post glacial sequences. Lineations of pockmarks are also present in these areas. These alignments usually reflect the position of the thickest sediments although some follow the trace of submerged channels that may have been the focus of organic rich sedimentation.

PETROLEUM GASES GENERATED FROM NATURAL OFFSHORE ASPHALT SEEPAGE IN SOUTHERN CALIFORNIA

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Natural hydrocarbon seeps are common in the shallow offshore Santa Barbara Channel and are significant sources of greenhouse gases. Recent attention has focused on gas emissions associated with oil near Coal Oil Point, California where oil and gas emissions are estimated to be from 16 to 95 m^3/day and 1 to 1.5 x 105 m^3/day respectively. A less studied but significant contribution is made by gases generated by oil dégradation resulting in impressive asphaltic seeps that occur offshore of Point Conception, and elsewhere in the Santa Barbara Channel, California. Here there are at least eight locales of coalescing asphalt mounds (breas) up to 18 m thick associated with gas seepage covering an estimated area of more than 10 km^2 . The asphalt volume estimate ranges from about 6.4 to 27 million m^3, or the volumetric equivalent of 40 to 170 million barrels of oil. The largest contiguous area near Point Conception covers about 2 km^2 and is as much as 10 m thick and occurs in water depths of 50 to 70 m. The individual mounds are typically 10 to 100 m in diameter but can be up to 250 m in diameter and formed from concentric flows of asphalt extruding from central and ancillary vents.

Geologically, the seepage of oil and asphaltic accumulations are well correlated with the oil-producing Monterey Formation. In particular, where the Monterey Formation has been heated, faulted, and often subcropping on the seafloor providing the oil source migration pathway, and reservoir. The oil, typically thermally immature and viscous, is biodegraded and continually restricts the flow from the underlying shallow reservoir by partially sealing the leaking reservoir resulting in the large asphaltic breas observed on the seafloor. Measuring the rates of gas and asphalt seep emissions is still an ongoing technical challenge, however the composition of the gases sampled from a variety of seeps demonstrate that the oil in the shallow subsurface has been anaerobically biodegraded resulting in the generation of carbon dioxide. In turn, methanogenic microbial processes resulting in secondary methane production have consumed some of that carbon dioxide.

This mineralization of oil can result in the consumption of up to 60 wt. % of the original oil with concurrent ^{13}C depletion of methane and ^{13}C enrichment of carbon dioxide. Analysis of gas emitted from asphaltic accumulations on the seafloor are up to 11% carbon dioxide with carbon isotopes as enriched as +24.0 ‰. Methane concentrations range from less than 1% up to 97% with isotopic compositions of between -34.9 to -66.1 ‰. Higher molecular weight hydrocarbon gases are present in highly varying concentrations reflecting both the thermogenic origin of the oil-associated gas as well as biodegradation, for example propane is preferentially biodegraded resulting in a carbon isotopic composition of -3.3 ‰. The loss of 60% of the original oil (170 million barrels) converted by microbes into methane or carbon dioxide results in an estimated release of up to 15 billion kg (~23 x109 m^3) of methane or 41 billion kg (~23 x109 m^3) carbon dioxide over the current lifetime of seepage. The maximum age of the seeps is likely no older than the Holocene based on geologic relationships and the terrestrial weathering rate of asphalt suggests a maximum lifetime of 1000 years. Thus, the seeps may contribute fluxes on the order of 15 (~23 x106 m^3) and 41 million kg (~23 x106 m^3) per year of methane or carbon dioxide, respectively, to the coastal ocean environment. The calculated daily emission rate (0.63 x 105 m^3/day) is comparable to those of Coal Oil Point and are can be a significant source of both methane and carbon dioxide to the atmosphere.

MICROBIAL COMMUNITIES IN THE SEDIMENTS OF THE RÍA DE VIGO, SPAIN

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The composition of the microbial communities inhabiting the anoxic sediments of the Ría de Vigo was investigated using pyrosequencing of 16S rRNA genes. A gravity core was taken in the innermost part of the Ría de Vigo (San Simón Bay) within a gassy zone at 10 m of water depth, providing 3.55 m of fine-grained sediments (muds) from the youngest seismic unit (4 m thick). Geochemical analysis shows high values of TOC (4 to 10%). Sediment and pore water analyses indicate a distinct sulphate-methane transition zone (SMTZ) between 60 and 80 cm where sulphate is depleted (to <1.7 mM) and methane increases (to >0.4 mM). The top of the acoustic turbidity (the gas front) at 80 cm corresponds to the lower limit of the SMTZ. The methane cannot have been derived from the underlying metamorphic and granitic rocks, but is probably derived by microbial degradation of the organic matter in the Holocene sediments.

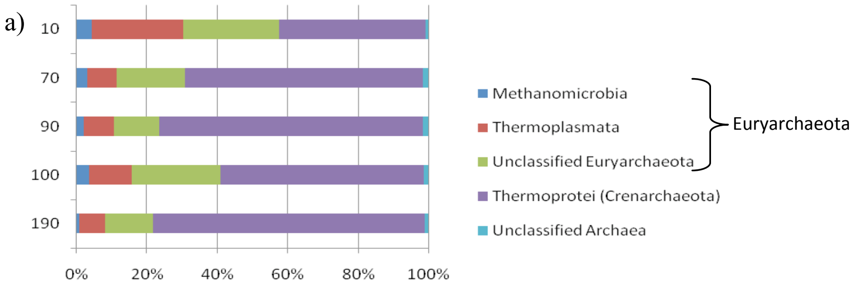
In order to investigate the microbial diversity above, within and beneath the SMTZ, samples at 10, 70, 80, 90 and 190 cm below the sea floor were taken. The DNA isolated from these samples was used to generate libraries of a 16S ribosomal DNA amplicon (V1-V3 hypervariable regions) by means of PCR amplification, performed using special fusion primers, and subsequent pyrosequencing using the Genome Sequencer GLX System. Different template-specific sequence primer pairs were used to analyse *Archaea* (A2F-519R) and *Bacteria* (27F-519R). After the application of the standard filters for pyrosequencing data using the Ribosomal Database Project (RDP) tools (Release 10), a total of 83,358 reads (Table 1) were included in the final analyses.

The taxonomical assignation performed by the online RDP Naive Bayesian rRNA Classifier shows that the most abundant group of archaea present in the sediments sampled are *Crenarchaeota* belonging to *Thermoprotei* class (Figure 1a). Only at the 10 cm level *Euryarchaeota* predominate over *Crenarchaeota*. In all cases class *Thermoplasmata* displays the higher frequencies among *Euryarchaeota* in contrast to class *Methanomicrobia*. A significant proportion of *Euryarchaeota* corresponds to unclassified reads, indicating the incomplete knowledge of the microbial communities in this kind of ecosystems. Among *Bacteria* (Figure 1b) phylum *Chloroflexi* clearly predominates over the rest of groups at all depths. Only at 10 cm phylum *Proteobacteria*, mainly class *Deltaproteobacteria*, reaches comparable values.

Comparisons between the number of clusters obtained at the 3% level of sequence dissimilarity and Chao1 estimates (Table 1), as well as rarefaction analysis results show that the microbial diversity was better sampled in the case of *Archaea*. Although there are differences in the microbial composition of the five sediment levels, trends along the area sampled were not clearly displayed. We just have observed a decreasing trend of the abundance of *Euryarchaeota* with depth, accompanied by an increasing presence of *Chloroflexi*, along with a general decrease in diversity values (Shannon index and evenness; Table1). The relationship between the SMTZ and the microbial organisms involved in the anaerobial oxidation of methane (AOM) will be discussed.

This investigation was supported by the "Ministerio de Ciencia e Innovación" of Spain thanks to grants CTM2009-13926-C02 and CTM2009-08158-E

Figure 1. Distribution of major microbial groups: (a) Archaea and (b) Bacteria.



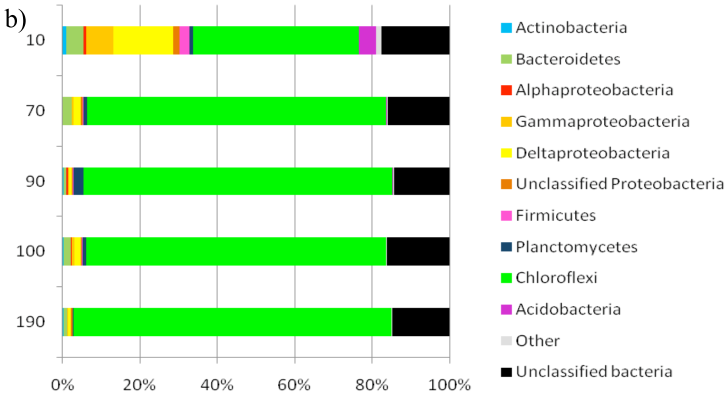


Table 1. Microbial richness and diversity indices.

	Depth	Reads	Clusters	Chao1	LCI95	UCI95	Shannon	Evenness
Archea	10	476	96	125.3	109.1	161.3	3.81	0.835
	70	1333	149	242.8	199.1	324.7	3.53	0.706
	90	991	106	202.3	153.2	302.5	2.98	0.640
	100	1347	143	239.0	192.7	328.4	3.47	0.700
	190	21622	487	680.7	616.0	777.9	3.43	0.554
Bacteria	10	617	336	1116.2	857.0	1504.3	5.44	0.935
	70	50503	2928	4758.8	4502.8	5056.5	5.51	0.690
	90	529	202	569.2	422.0	815.0	4.63	0.872
	100	2662	525	1100.7	942.4	1319.1	4.92	0.786
	190	3278	497	994.5	851.4	1195.3	4.80	0.774

TEMPORAL EVOLUTION OF THE MACRO-FAUNAL DISTRIBUTION AT THE REGAB POCKMARK IN THE NORTHERN CONGO FAN, BASED ON VIDEO-MOSAIC ANALYSES

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The Regab pockmark is an 800 m-large circular depression on the seafloor located on the passive Congo-Angola margin and in the vicinity of the Congo deep-sea fan. The system is characterized by the presence of methane-rich fluids in the sediments. Anaerobic oxidation of methane (AOM) in the subsurface produces sulfide and allows sustaining rich and abundant chemosynthetic communities. The dominant megafaunal communities présent at Regab are dominated by symbiont-bearing taxa including Siboglinidae, polychaetes, two species of Vesicomyidae clams, and the mussel *Bathymodiolus aff. boomerang*, forming a mosaic of biogenic habitats. Cold-seep systems and their associated chemosynthetic communities have been the focus of many studies, but little is known about the temporal evolution of the faunal distribution in such systems. Getting a better knowledge of the community dynamics is important since changes in distribution are also believed to reflect changes in seepage flow or chemistry.

During the West African Cold Seeps (WACS) cruise in 2011, the Regab pockmark and its main faunal assemblages were intensively surveyed using the high-resolution color cameras mounted on the Ifremer's remotely operated vehicle (ROV) Victor 6000. The imagery data allowed building a high-resolution video-mosaic, which fully covers a 13,500 m^2-large rectangular area of the seafloor. The mapped area is located towards the center of the pockmark and is where chemosynthesis-based megafaunal communities are most abundant. The video-mosaic was constructed with the Ifremer MATISSE program and geo-referenced into geographic information systems (GIS), and the main faunal assemblages and carbonate concretions were mapped, allowing precise area calculations and density estimations. Based on previous imagery data of the same area, collected during the Biozaire cruise in 2001, and related faunal distribution analyses1, we propose a comparison of the faunal distribution at the Regab pockmark. The results presented include a description of the 10-year evolution of the main chemosynthetic assemblages and the associated maps of faunal distribution.

Acknowledgements: the WACS cruise was supported by Ifremer (chief scientist K. Olu). We thank the captain and crew of the N/O Pourquoi Pas? and the ROV Victor 6000 team. This work is supported by the European Commission under the EU Framework 7 funded Marie Curie Initial Training Network (ITN) SENSE net (contract nº237868).

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MONITORING POCKMARKS IN AN ENCASED VALLEY (RÍA DE VIGO, NW SPAIN)

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Ría de Vigo is the most southerly of the Rías Baixas (Galicia). The Ría de Vigo's physiography presents a distinctive funnel shaped; with an area extend of 176 km^2. San Simón Bay is a small shallow basin located in the innermost part of the ría. This Bay is connected to the ría by a narrow channel, Rande Strait. This ría present islands at it mouth (Cies Islands) that confer some protection to Atlantic storms (Fig. 1). Galician Rías have a high productivity in their waters due to upwelling processes that take place in the western margin of the Iberian Peninsula. This high productivity makes the rías a good place to aquaculture, especially mussel farming. Mussel's rafts have been an important source of organic matter to the seafloor over the last 60 years. This organic matter is susceptible to generate methane through microbial degradation.

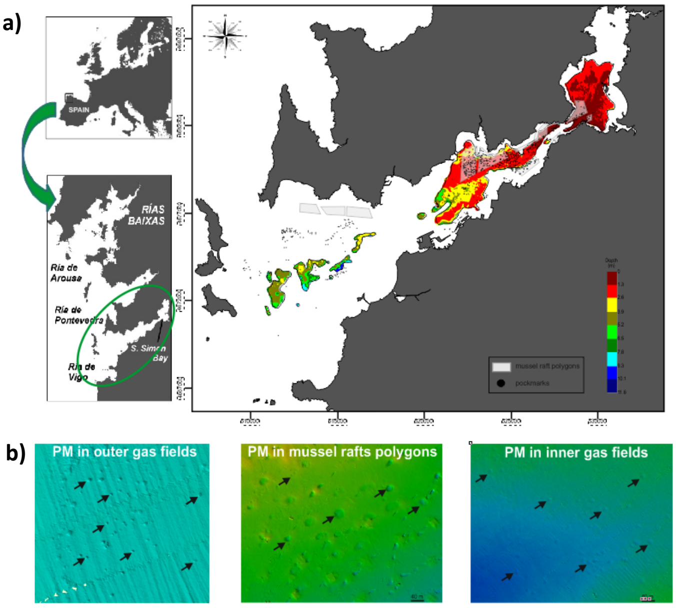

Figure 1: a) Location of the study area: the ría de Vigo. The map shows the position of the gas fields as well as the mussel rafts polygons. b) Multibeam image of several pockmarks.

Different seismic surveys conducted in the Ría de Vigo allow identified several gas fields along the ría (Fig. 1). The depth at witch these gas fields appear is shallower in the inner part of the ría (lower than 1 m) and increase towards the outer part (since 1 to 7 m). In areas where mussel rafts debris appear the gas front is nearer the seabed.
A detailed multibeam mapping (grid of 1x1 m) together with high resolution seismic records obtained until present-day have allowed to identify more than 800 pockmarks in the Ría de Vigo, most of which are in the middle-inner ría (see Figure 1). Some pockmarks present acoustic plumes rising from the seafloor, indicating that at acquisition time those were active.

In the middle-inner part of the ría, pockmarks are located over the gas fields or in their vicinity. In the outer part of the ría, pockmarks are situated towards the northern side of the ría outside of the mapped gas fields. The biggest pockmarks are located in the mussel rafts areas and towards the entrance of the San Simón Bay. These pockmarks are greater than 25 m diameter. The smaller pockmarks (5-25 m) are distributed over the ría. However, most of pockmarks situated in the outer part of the ría are smaller than 10 m.

The biggest pockmarks are sited in areas where gas front is closer to the seabed and the input of organic matter is very high. The accumulation of gas methane so close to the seabed, together with changes in the temperature and the hydrostatic pressure (due to tidal variations) may trigger the violent gas expulsion.

Smaller pockmarks, especially those located outside the gas fields, could be due to the fluid migration using permeable pathways and minor fractures. In addition, some pockmarks are found along trawl-gear marks which must have disturbed the permeability conditions of the surface seafloor sediments.

In order to identify possible changes, i.e. in the size, shape, number or position, in the pockmarks along the time, an area of 2.56 km^2 was monitored using a multibeam Eco sounder during three consecutive years. The first survey was conducted in September 2009, another in November 2010 and the last one in June 2011. During the first survey, 206 pockmarks were identified and 224 and 230 were mapped in June and November 2010 surveys, respectively. These pockmarks are always located over the gas field or in its vicinity. There are also a large number of pockmarks located in the central part of study area. In seismic records acoustic turbidity placed nearer the seafloor is observed.

Along these three years no significant differences in size neither in shape (between the size and morphology) of the pockmarks were observed, suggesting a high potential of preservation. New small pockmarks were formed during these years. A total of 19 pockmarks have appeared between September 2009 and November 2010 and only 6 appeared between November 2010 and June 2011. This high preservation is interpreted as due to low sedimentation rates (2 gr DW m^{-2} d^{-1} in the channel, Alonso-Pérez et al., 2010) combined with low bottom current velocities inside the Ría de Vigo (0.05 m s^{-1}, Torres López et al., 2001) and the cohesive muddy facies of the present seabed.

Acknowledgements:

This work was funded by the Ministerio de Ciencia e Innovación (MICINN) under research projects CTM2009–13926-C02-01 and CTM2009-08158-E, and by Xunta de Galicia project 10MDS310020PR. N. Martínez-Carreño was funded by the FPI research grant from MICINN. We would like to thank Seismic Micro-Technology Inc., who provided free licences of Kingdom Suite software.

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CHEMICAL AND ISOTOPIC COMPOSITIONS OF GAS HYDRATE WATERS RETRIEVED FROM KUKUY K-9 MUD VOLCANO IN LAKE BAIKAL, RUSSIA

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The Multi-phase Gas Hydrate Project (MHP) is an international collaborative effort by scientists from Japan, Russia and Belgium to investigate natural gas hydrates that accumulate in the subsurface of Lake Baikal. In 2010, a field operation of the MHP-10 project was conducted. GH-bearing and -free sediment cores were retrieved using gravity corers from a mud volcano named Kukuy K-9 in the central basin of Lake Baikal.

A piece of agglomerated GH was dissociated on board RV Vereshchagin just after its retrieval. It was dissociated in a closed chamber filled with inert gas under atmospheric pressure and room temperature. The chemical and isotopic compositions of the water samples were measured to investigate changes occurring during sequential GH dissociation.

The concentration ratios of hydrogen carbonate ions, chloride ions, and sulfate ions in the GH waters were not consistent with those calculated by simulation based on mixing of pore water and lake bottom water, suggesting that the ions detected in the GH waters did not originate from the contamination of pore water and lake bottom water during core retrieval and handling. The stable isotopic ratios of oxygen and hydrogen remained constant for all of the fractions during sequential GH dissociation, and they were higher than those of the lake bottom water and pore water.

The finding that the chemical and isotopic compositions do not show any apparent contamination of pore water and lake bottom water on the GH waters indicates that ions as well as water molecules detected after retrieval already existed in the agglomerated GH. The sampling and chemical/isotopic analysis of GH waters without any contamination is expected to be an important tool in the discussion of the formation mechanism of GHs in the Kukuy K-9 mud volcano.

RECENT RESERVOIRSOF METHANE INSIDE SAN SIMON BAY (RÍA DE VIGO, NW IBERIA): ASSESSING ITS SEDIMENTARY ENVIRONMENTS AND AGES OF FORMATION

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Ría de Vigo is a river valley flooded by the sea, with a bay (San Simón Bay) at its innermost part. The accumulation of Holocene sediments containing shallow gas in San Simón Bay has been attemptedby the integration of multidisciplinary studies that comprised geophysical, geochemical, radiocarbon and micropaleontological analyses. Subsequently this new information was compared and correlated with otherdata obtained out of the Rande Strait andin the current Cesantes beach (Fig. 1).

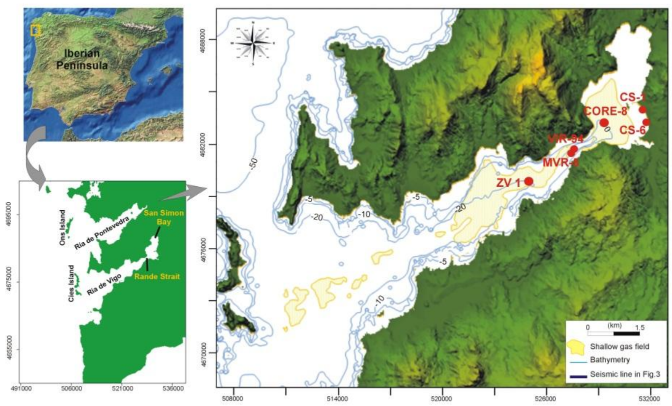

Fig. 1: Ría de Vigo, NW Iberia. Study area and discussed sites.

Most of the seismic records inside the bay are obscured by acoustic turbidity which represents gassy sediments. These gas reservoirs are enclosed into the uppermost seismic unitcorresponding with highest sea level (HST). However, other types of analyses were necessary for getting higher resolution. Several cores (CORE-8, VIR-94, MVR-5,ZV-01) and two beach trenches (CS-1 and CS-6) were performed in the area (Fig 1).Their analyses included detailed geochemical studies, grain size determinations,and also qualitative and quantitative studies of pollen,dinocysts and other non-pollen palynomorphs (NPPs) in the sediments.Therefore, the chronologyof the corers wasfinally based on the radiocarbon dating combined with the pollen markers and historical informationpreviously used by Muñoz Sobrino*et al*. (2012).

A gravity core (CORE-8)taken within the gassy zone inside the San Simón Bay,at 10 m water depth, provided 3.55 m of fine-grained sediments (muds) from the youngest seismic unit (at least 4 m thickat the edge of the basin).Radiocarbon dating of a shell and palynomorphs analyses performed on a twin corer (3.56 m) led us to estimate the age of its base about 1200 cal. yr BP. Palynomorphs analyses confirm that its organic matter content have a mixed marine-continental origin,despitelocal marine conditions weredominant. Furthermore, prevailing downwelling conditions may be deduced along this period, with only a prominent hydrological change recorded between 70 - 150 cm depth, a period of increasing upwelling and coarser grain sedimentation that has been identified as the Little Ice Age (LIA: *ca*. 350-530 cal. yr BP).

Geochemical analysis show high values (4 to 10%) of TOC. Sediment and porewater analyses indicate a distinct sulphate-methane transition zone (SMTZ) at 60 - 80 cm depth, dated as younger than 380 cal. yr BP. The top of the acoustic turbidity (the gas front) is located at 100 cm below present sea bed (b.p.s.b.), close to lower limit of the SMTZ (García-Gil *et al*., 2010). This point was dated *ca*. 450 cal. yr BP in the core. Therefore, the gas reservoirs existing in the top of uppermost seismic unit in San Simón Bay are relatively recent, enclosed in sediments dated between 450-1200 cal. yr BP but extending older towards the base of the seismic unit.These results are consistent with those obtained in a second gas field out of the Rande Strait (vibrocore ZV-01, Fig. 1), where the acoustic gas front is placed at 140cmb.p.s.b., and the age of the gassy sediments estimated as older than *ca*.550cal.yr BP.

The minimum age for the base of the HST seismic unit that contains the gassy sediments in the internal part of the riamay be at least 4500 cal. yr BP(Muñoz Sobrino*et al*. 2012).Nevertheless, new seismic and radiocarbon data obtained at the mouth of the bay (MVR-5, Fig. 1) suggest that it could be extended until 7500 cal. yr BP. Even so, several distinctive environmental changes occurred in the area during the Mid- and Recent Holocene. Particularly, two different organic horizonshave been found in Cesantes beach, corresponding with: 1) a marine/estuarine muddy sediment dated *ca*. 3150 cal. yr BP; and 2) a freshwater logged pond that has been dated towards the end of the Roman Period (1700-1400 cal. yr BP).These and otherstagesrecognized in the sedimentary record of the bay (e.g. 2.8-Event) agree with the environmental trends previously described in this region (Muñoz Sobrino*et al*. 2012) andsurely affected the coastal ecosystems. Therefore, they could also have some influence in the genesis and preservation of gas in some of the shallower areas of the ria.

Acknowledgements:

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BIOGEOCHEMICAL CHARACTERISTICS OF METHANE DISTRIBUTION IN SEDIMENT AT THE GAS SEEPAGE SITE OF SEVASTOPOL COASTAL AREA

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CH_4 concentration data and the rates of microbial processes of carbon and sulfur cycling occurring in bottom sediments from Sevastopol coastal area (Black Sea) were obtained in October 2011. From previous studies, a several sporadically active methane seeps had been documented here, locating mainly along the lines of geodynamic faults. During the research expedition intense release of gas bubbles from sediments was observed by echo-sounder SeaCharter 480 DF, representing more than 20 single gas flares. According to the diagram of the bubble rise velocity vs. its radius (Patro et al., 2001) bubble diameters were defined about 1.1 - 1.3 mm. Vertical profiles of CH_4 concentration evidenced that cold gas seepages in the Sevastopol Bay caused by penetration of the methane from the deep sedimentary layers into the subsurface horizons. Concentration of methane dissolved in near-bottom and pore waters at seepages site as well as CH_4 oxidation rates in bottom sediments were statistically higher than at the background areas. In all investigated sediment columns (30 cm bsf) methane oxidation rates exceed intensity of microbial methanogenesis. The highest sulfate reduction (SR) rates detected in the subsurface sédiment layers of Sevastopol coastal area (up to 92.5 µmol dm^{-3} day^{-1}). It was showed that methanogenesis processes occurring in the underlying organic-rich sediments were account for high content of dissolved methane in subsurface sediments at Streletskaya Bay, at that CH_4 production by acetoclastic methanogens was essentially higher in comparison with hydrogenotrophic methanogenesis (up to 80% from the total methane production).

This study was supported by the Russian and Ukrainian Foundations for Basic Research (projects N F40.6/006; 11-04-90402- Ukr_f_a).

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FLUID SEEPAGE INDICES ON TOFIÑO BANK, ALBORAN SEA

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In the Alboran Sea, several colinear ridges ("Alboran Line") separate the West and South Alboran basins. While the South Alboran basin is characterised by an intense igneous activity, the West Alboran basin, mostly non-volcanic and characterised by a large Neogene depocentre, shows numerous diapir and mud volcanoes. One of these mud volcanoes is presently the only active seeping feature observed in the Alboran Sea.
The Alboran Line is formed from NE to SW by the Alboran Ridge, the South Alboran Ridge, the Tofiño Bank and the Xauen Bank. All these features show flat abraded summits topped by mainly calcareous sediments. However, Alboran Ridge is a volcanic ridge, while Xauen bank is a fold and thrusted sedimentary structure. The three summits constituting the Tofiño Bank are located in between at the intersection of the Alboran Line and the offshore continuation of the N30°E trending Al Idrissi fault zone.
We present new intermediate and high resolution seismic data, multibeam bathymetry and visual observations on and near the Tofiño bank collected during the Marlboro 1 and 2 and Saras cruises in 2011 and 2012. Our data reveal that the area is characterised by ancient and active transpressive deformation associated with mass-movement deposits and contourites sedimentation. A preliminary analysis indicates the presence of fluid seepage features on the Tofiño Bank. On top of the central summit, at a water depth of only 70m, an acoustic flare was detected and free gas escape (bubbles) was observed at the sea surface. Northeast of this summit, another site showed a clear acoustic chimney within the surface sediments. The different data sets are discussed in order to evaluate these potential sites of active fluid seepage. Due to its location in one of the most tectonically active areas of Alboran Sea and at the intersection of two major fault zones, Tofiño bank appears as a favourable zone for fluid migration and seepage.

MOLECULAR AND ISOTOPIC COMPOSITION OF HYDRATE-BOUND AND DISSOLVED GASES IN THE CENTRAL BASIN OF LAKE BAIKAL

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Lake Baikal, Russia, is one of the most attractive gas hydrate study-areas since the first gas hydrate in fresh water environment was retrieved from the sub-bottom depths of 121 and 161 m and later from the subsurface of the lake floor (near the bottom surface). A lot of studies to figure out the origin of the gases incorporated in and/or bound to gas hydrates have been carried out and reported, e.g., Hachikubo et al [Hachikubo, 2010]. Gas analysis is one of the basic measurements of sediment cores for gas hydrate studies.

We conducted surveys during the MHP-11 (Multi-phase gas hydrate project) cruise VER-11-1 to the central basin of Lake Baikal in June 2011. Sediment cores were retrieved from Kukuy Canyon area (K0, K3, K4, K5, K6, K7, K10, K11, K12), Novosibirsk, and some anomaly points (Krest, Ulan-Nur, P19, P20, etc.) in the central basin of Lake Baikal. Gas hydrates were found in 11 cores during the cruise. 6 cores with gas hydrates of them were retrieved at new five points (K4, K11, K12, Krest and seep 13). We obtained the samples of hydrate-bound gas and dissolved gas in pore water on board. Molecular compositions of hydrate-bound gases were measured on board the ship and at our laboratory in Kitami, Japan. The results of both measurements were almost the same. We investigated stable isotope compositions of them. Molecular and stable isotope compositions of dissolved gas in pore water were measured at our laboratory. We report on the concentration-depth profiles of méthane in dissolved gas and the gas compositions of methane and other hydrocarbons in hydrate-bound gases. By the way, when the surrounding gas of the gas hydrate formed in one system is replaced with different gas of stable isotope compositions from the original gas, it is possible that the stable isotope compositions of hydrate-bound gas are changed. We investigated by methane hydrate about that.

COHESION FORCE MEASUREMENT OF METHANE HYDRATE

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In oil or gas industries, hydrate particle aggregation occasionally causes serious pipeline obstruction. The cohesion force of hydrate is considered to play an important role in this aggregation. So far, such forces have been investigated for gas hydrates other than methane hydrate, as far as the authors know. Moreover, the contact area of hydrate clusters has never been taken into account. In this study, the cohesion force of methane hydrate per unit area is obtained by neatly designed experiment.

Fig. 1 shows the schematic view of the experimental apparatus used in this study. Methane gas is injected into the high-pressure vessel, which is set under the so-called hydrate stability condition of pressure and temperature. The present measurement procedure follows.

1. Two cups filled with methane hydrate are set in the vessel: one is upside and the other is downside.
2. They are in contact with a preset force for a preset time.
3. They are pulled apart with constant speed and their cohesion force is measured by a load cell.

This was conducted under various conditions of contact force, contact time, pressure, and temperature. The obtained results indicate that the cohesion force of methane hydrate increases with the contact force and the contact time. Temperature is particularly influential when it is closed to the equilibrium temperature at a set pressure.

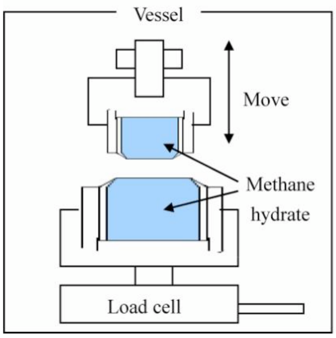

Fig. 1 Schematics of experimental set-up

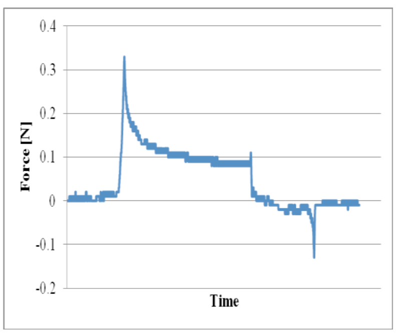

Fig.2 A result obtained from an experiment

SEEPAGE AND GAS FEATURES IN DUNMANUS BAY, IRELAND

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An acoustic survey of Dunmanus Bay, Ireland in 2007 conducted as part of the INFOMAR project (Integrated Mapping for Sustainable Devolpoment of Ireland's Marine Resources) revealed a small pockmark field and numerous sub-surface signatures typical of shallow gas accumulations. Vertical acoustic signatures observed in the water column suggested that some of these pockmarks might be actively venting gas. In 2009 and 2011 the site was revisited and numerous water column and sediment core and grab samples were collected. In-situ methane concentrations were measured with a METS sensor. Furthermore, the composition of benthos was examined to assess whether the presence of gas affects benthic communities.

Dunamnus Bay is a fjord-like setting with only one small river draining into the Bay. Salinities are comparable to that of the open ocean and varied sligthly around 35 psu. The seabed sediments in the Bay are predominantly muddy sands with a small gravel component. Although acoustic data suggests that shallow gas is present in multiple locations throughout the bay pockmark features are only observed in sediments with a high silt/clay content (~30%). Dunmanus Bay field contains 60+ pockmarks that reach up to 20 m in diameter and range from 0.3 to 0.8 m in depth. Pockmarks occur in clusters of 5-9 larger features with small, random satellite pockmarks (1-2 m wide) in the vicinity of these clusters. The clusters appear to be parallel to each other however the entire field shows a clear NE-SW orientation limited by two rock outcrops and parallel to the main Dunamnus Fault crossing the Bay. The concentration of methane in the water column ranged from 5.1 to 14.2 nM directly above the features (3m) and from 1.3 to 7.7 nM across the remainder of the water column. These values are close to background levels and thus suggest that venting observed in the acoustic data sets is of low intensity and that released methane is quickly dispersed in the water column. Sediment cores collected from areas characterized by acousic turbidity in the sub bottom profiles confirmed the presence of methane gas in the sediment in low µM levels. The concentration of gas was higher in more porous sand enriched layers. Such layers often offer the least resistant pathway for migrating gas bodies and facilitate laterall spreading of gas when upward migration is impeded. The source of the Dunmanus Bay shallow gas remains unknown and is yet to be confirmed by isotpic studies. Sulphate reduction was not complete in any of the analysed cores thus observed methane could not be generated in situ via microbial methanogenesis in the top 6m of the seabed and must have migrated from a deeper source.

Benthic community structure in the pockmark area compared to controls had on avergage lower richness, eveness and diversity of species however no major differences were observed. The main species recorded were typical for this region; polychaetes, crusteceans, molluscs and echinoderms. Species typically flourishing in actively venting sites were not observed in Dunmanus Bay which further suggests that macrobiota do not benefit or directly rely on emitted methane as a carbon source.

LONG-TERM METHANE RELEASE FROM THE SEABED: BENTHIC FORAMINIFERA RECORDS FROM THE SVALBARD MARGIN, FRAM STRAIT

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The Vestnesa Ridge is a 100 km long sediment drift in the Fram Strait and represents one of the northernmost gas hydrate provinces that exist close to a sedimented ocean ridge. One of thecores,as well as surface sediment samples collected from Vestnesa Ridge (west of Svalbard at ~79°N) from a water depth of ~1200m in an area with several active methane gas flares are presently investigated.

The central science objective is to examine the release of free and dissolved CH_4 gas into the ocean on benthic foraminifera. The ongoing project will resolve the frequency of CH_4 emissions from the seafloor through time in relation to past climate change. Benthic foraminifera are an important component of seafloor communities, and are important as direct bioindicators of physico-chemical conditions at the sea-bottom and bottom water. Numerous species of benthic foraminifera have been found in different methane rich marine settings and have proved to be good biosensors of methane releases as they prefer to feed on rich bacterial food sources at methane seeps. The distribution patterns of benthic and planktic foraminifera species and $\delta^{13}C$ signature in their shells together with other geochemical, sedimentological and physical parameters is investigated.

The magnetic susceptibility record of the control core shows a pattern with values typical for the western Svalbard margin (Jessen et al., 2010) that covers the last c. 30,000 years. The core from the active seep area shows almost constant values of very low magnetic susceptibility. Based on radiocarbon dating it is shown that the record also covers the last c. 30,000 years. The core is characterized by a strong H_2S odour in the upper part with numerous gas bubbles present in the sediment. A distinct layer of large bivalves dated 18,000 years BP probably marks the time when the seep became more active. The modern samples (retrieved by multi-corer) cover two different habitats within the methane rich environment: bacterial mats and tube-worm fields (Pogonophora), as well as a control sample from outside the methane seep sites.

Reference

Jessen, S.P., Rasmussen, T.L., Nielsen, T., Solheim, A., 2010. A new Late Weichselian and Holocene marine chronology for the western Svalbard slope 30,000 - 0 cal years BP. Quaternary Science Reviews 29, 1301-1312. doi: 10.1016/j.quascirev.2010.02.020.

LATTICE BOLTZMANN SIMULATION OF GAS-WATER TWO-PHASE INTERFACE AND ESTIMATION OF RELATIVE PERMEABILITY IN SPHERICAL GRAIN SEDIMENT

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CO_2 storage in the form of gas hydrate is one of the CCS methods. CO_2 hydrate is considered to form mainly on gas-water interface. Therefore, the accurate evaluation of the interfacial area is required to predict the quantity of produced hydrate. In this study, an algorithm to compute the area of gas-water two-phase interface is incorporated into a lattice Boltzmann method and the interfacial area and the relative permeability are calculated. Then, they are compared with the solutions of theoretical model equations. Fig. 1 shows the interfacial areas calculated with the present simulations and the theoretical equation proposed by Peng and Brusseau (2005). The areas of the present simulations are in moderately good agreement with those of the model equation. The comparison of the relative permeabilities calculated with the present simulations, the Brooks-Corey equation (1964), and the Van Genuchten (1980) is illustrated in Fig. 2. They show the same trends that the water-phase relative permeability increases and the gas-phase relative permeability decreases with water saturation.

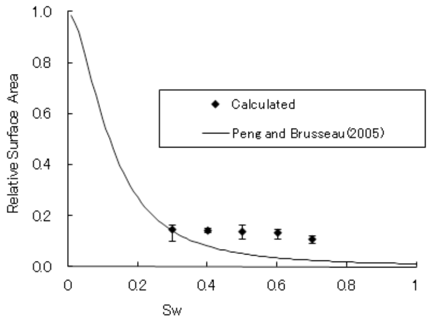

Fig. 1 Calculated interfacial areas

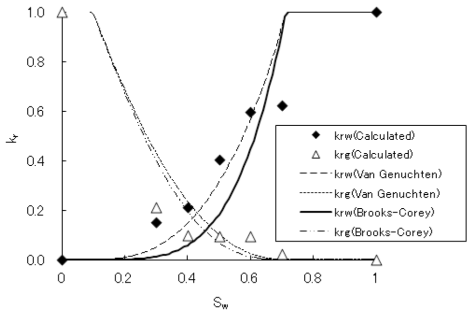

Fig. 2 Relative permeability

HIGH-RESOLUTION SEISMIC STRUCTURES LINKED TO AN ACTIVE MUD VOLCANO OFF SW TAIWAN

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Because of wide spread distribution of bottom simulating reflectors (BSR), the area off SW Taiwan is considered as a high potential gas-hydrate formation area. At water depth sallower than ~600 m, the BSR disappears and gas hydrate dissociates. Thus, in the near shore area to onshore of Southern Taiwan, the marine sediments bear a large quantity of gas. The gas (fluid) has migrated upward and created many diapiric structures and mud volcanoes. To better understand the features of gas seepage and fluid flow at an active mud volcano, we conducted the deep-towed side-scan sonar (SSS), sub-bottom profiler (SBP), and multi-channel reflection seismic (MCS) surveys around the mud volcano MV1. The seafloor features and sub-bottom structures identified in the study reveal pockmarks, mud diapirs, authigenic carbonate and acoustic transparent zones. In addition, the survey profiles show structural faults which may provide pathways for the upward migration or eruption of fluids and argillaceous materials from the seafloor. Active venting of gas at MV1, at a water depth of about 450m, the emitting gas could even form a clear gas plume imaged by the EK 500 echo sounder. The active state of the mud volcano can be inferred from these gas plumes. Based on the MCS results, we can find a mud diapiric structure beneath the mud volcano. Furthermore, the seabed above it usually has a flow-like morphology. The blanking of the signal may indicate the gas-bearing sediments. The enhanced reflections are usually below it. These phenomena may occur because of the différence in reflection coefficients between formations with and without gas. Submarine landslides could be due to the slope instability in the seafloor caused by the dissociation of the gas hydrate.

3D MULTICHANNEL SEISMIC INVESTIGATION OF ACTIVE POCKMARKS IN THE LOWER CONGO BASIN

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The continental slope in the Lower Congo Basin is dominated by active salt tectonics induced by the downslope movement of Aptian salt deposits. This process leads to prominent deformation of the overlying sediment column, including extension upslope and compression downslope. Additionally, the Congo River is a source for large volumes of sediment from the African continent that are deposited on the slope, and since the Upper Miocene predominantly in the Congo deep sea fan. The area north of the Congo Canyon is characterized by a relatively smooth seafloor although large scale deformation by salt tectonics can be observed in the sub-seafloor. Salt tectonic activity is responsible for creating widespread pathways for hydrocarbon migration from pre- and post-salt source rocks. Additionally, biogenic formation of methane occurs in organic-rich sediment at shallow depths. Both sources of gas and fluids contribute to the widespread occurrence of seafloor seepage in the Lower Congo Basin.

During R/V Meteor Cruise M56, a high resolution 3D multichannel seismic dataset was acquired over two active pockmark features north of the Congo Canyon. The pockmarks show active seepage, evidenced by acoustic flares in the water column signifying gas bubble streams. Additionally, seepage related biogenic communities, authigenic carbonates and gas hydrates were recovered from these sites. Seismic data show chimney structures underneath the topographic expressions at the seafloor that connect the seafloor to interpreted gas-bearing sedimentary strata in few hundred meters depth.

The 3D multichannel dataset allows for the detailed study of the sub-seafloor structure of these seepage sites. We plan to present insights into the small-scale structure of pockmark features. Especially the relation to hemipelagic and turbiditic sediments in the area as well as the link to migration pathways like faults will yield information about the governing factors of seepage location in the area. Previous studies suggest that polygonal faulting in the otherwise sealing hemipelagic sediments facilitate the ascent of gas to the seafloor from deeper strata and thus focus pockmark formation to fault planes or intersections. Furthermore, gas reservoirs can be observed within 300 m below the seafloor and possibly also at shallower depths. High amplitude seismic signatures are widespread in the area in few hundred meters depth and can be interpreted as gas charged sediments. Many pockmark features in the area appear to be connected to such strata and our detailed study will investigate the relationship of seepage features at the seafloor to such reservoirs in shallow depths.

INTERACTION OF GAS MIGRATION, HYDRATE FORMATION AND SEDIMENTARY PROCESSES IN THE KERCH FLARE AREA, BLACK SEA

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During R/V Meteor Cruise M72/3 in March/April 2007 to the Eastern Black Sea a set of 2D high resolution seismic profiles were acquired near the Kerch peninsula. In the vicinity, the Kerch gas flare of more than 400 m height above the sea floor was observed in a water depth of 900 m, which is located within the gas hydrate stability zone (GHSZ). A large number of gas flares appear shallower than approx. 700 m water depth above the upper boundary of the GHSZ. Where water is deeper than 700 m, many shallow bright spots can be found in the sub-seafloor, but only a single group of gas flares was found so far. The gas might originate from deeper gas reservoirs, which are known from deep seismic studies, migrate along faults above anticlines, as well as along sediment strata towards the upper slope, where leakage is not inhibited due to the absence of gas hydrates. A conceptual model will be presented to illustrate the mechanisms of migration and seepage.
The Kerch gas flare is located above an East-West oriented anticline, which formed as a result of compressional events. Bright spots and high amplitude reflector packages also can be observed both in and above the anticline structure which are interpreted as the evidence of free gas traps. Some deep faults cut the flanks or top of the anticline and reached to the upper sediment layers. Potential pathways were provided by these faults for gas/fluid upward migration. Although the anticline is located beneath the GHSZ, a bottom simulating reflector (BSR) could not be clearly identified, which indicates a limitation in trapped free gas. On the other hand, bright spots do indicate free gas migration and trapping, and their upper limit may hint to the base of the gas hydrate stability zone (BGHSZ).
As terrigenous sedimentation is characteristic for the uppermost sediment units, high permeability in coarser layers may support upslope gas migration along strata which diverts gas flux toward shallower depth, and interbedded finer layers may have inhibited further vertical migration.
As an anomalous situation, we think that the Kerch gas flare is located, where the sedimentary deposits are unstable, the seal by finer layers is not efficient and higher amounts of gas support leakage toward the sea floor and across the GHSZ.

STRUCTURE OF JELLYLIKE BIOFILMS NEAR THE SITE OF METHANE SEEP ST. PETERSBURG (CENTRAL BAIKAL)

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During the dives of deep-sea manned submersibles "MIR" in 2010, jellylike biofilms were discovered above gas-hydrate field in Central Baikal (methane seep St. Petersburg). These biofilms formed small fields (approximately 1 m^2 in diameter) above thick layers of methane hydrates. The water squeezed out of them had different chemical composition compared to near-bottom water and sediment pore waters. It contained higher ion concentrations of iron, chlorine, and bromine. Light, epifluorescence, and scanning microscopies allowed us to identify in the biofilms many diatom valves and morphologically diverse mucoid microorganisms.

We have extracted total DNA from the biofilms. Phylogenetic analysis of 16S rRNA gene fragments has shown low bacterial diversity; representatives of the phyla *Gammaproteobacteria*, *Betaproteobacteria*, *Verrucomicrobia*, *Bacteroidetes*, and *Firmicutes* were observed. Most sequences were similar to obligate gram-negative methylotrophic bacteria of *Methylophilacea* family, the genera *Methylophilus* sp. (96%) and *Methylotenera* sp. (99%), mainly using methanol and methylamine as substrates. Moreover, DNA of some biofilms was found to contain sequences of the class *Gammaproteobacteria* which are most similar to the representatives of the genus *Methylobacter* (95%) and those of the order *Methylococcales* (95%). Several sequences belonging to the class *Betaproteobacteria* were similar to the bacterial sequences participating in iron cycle. Comparison of archaeal 16S rRNA gene fragments has shown four sequence types which were similar to uncultured *Euryarchaeota* isolated from the alpine lake Llebreta (99%).

Presence of the functional genes, *pmoA* and *mxaF*, providing gradual methane oxidation to carbon dioxide have been determined using specific primers. Structural analysis of the gene *pmoA* indicate the presence of type I methanotrophs which are most similar to the species *Methylobacter psychrophilus* and uncultured sequences of the class *Gammaproteobacteria*. Sequences of the gene *mxaF* encoding subunit of methanol dehydrogenase have shown close similarity to the species *Rhodanobacter sp.* and *Methylovulum miyakonense.* Additionally, in total DNA we have detected the gene *rusA* encoding reduced protein of iron ions. Among the obtained sequences of the gene *rusA*, we have identified several sequence types, one of which formed a separate cluster in the phylogenetic tree that is in the same clade as sequences of the uncultured *Thermodesulfobacter* (91% similarity). In total DNA, we have also detected representatives of the phylum *Planctomycetes* participating in anaerobic ammonium oxidation and uncultured *Verrucomicrobia* (88-99%) which representatives are capable of methane oxidation under anaerobic conditions. Using primers, we have not received a positive signal for methyl coenzyme reductase (gene *mcrA*) and genes *dsrAB* and *nifH* providing sulphate reduction and nitrogenase activity.

Therefore, the obtained data indicate that jellylike biofilms near the near-surface occurrence of methane hydrates form a consortium of aerobic and anaerobic microorganisms which possess fermentative systems facilitating formation and oxidation of methane.

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