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Fluid seepages / mud volcanism in the Mediterranean and adjacent domains

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A collection founded and edited by Frédéric Briand.
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1. INTRODUCTION: WORKSHOP OBJECTIVES AND OUTLINES

The workshop took place from 19 to 22 October 2005 in Bologna. Sixteen scientists from eight countries (see list at the end of the volume) attended the seminar convened at the invitation of CIESM. They were welcomed by Drs Frederic Briand, Jean Mascle and Dimitris Sakellariou, who recalled the main objectives and background of the meeting and expressed their appreciation for the top-quality logistic assistance provided by Dr Rossella Capozzi.

The workshop was dedicated to a critical review of our geological/geophysical knowledge on fluid seepages and related features (mud volcanoes, gas chimneys, gas plumes, authigenic sedimentation) and associated processes in the Mediterranean Sea, and in the Gulf of Cadiz and the Black Sea, its western and northeastern provinces. The consequences of fluid seepage on the deep biological environments, a subject of obvious importance, was deliberately left out of the discussions as it will be covered in a future CIESM workshop.

Why is the Mediterranean Sea region a unique place to study cold seeps?

In the early '80s Italian researchers followed a few years later by scientists from the Tredmar program (Moscow State University and Unesco) described mud diapirs or volcanoes (MV) and mapped several MV fields on top of the Mediterranean Ridge in the Eastern Mediterranean. By the late '90s systematic swath mapping (mainly, but not only, conducted by French laboratories) demonstrated the widespread occurrence of CS/MV in different geodynamic settings of the Mediterranean domain, from active to passive margins. Russian and German surveys discovered at the same time many fluid-releasing features in the Black Sea, while a consortium of European institutions initiated detailed studies of MV fields previously discovered by US scientists in the Gulf of Cadiz just at the western boundary of the Mediterranean Sea. It is by now well admitted

Fig.1. Location of the main MV provinces discussed during the workshop.

that the convergence zone, extending over almost 5,000 km long, from Azerbaijan over the Black Sea and the Mediterranean Sea to the Gulf of Cadiz and forming the contact between the progressively colliding African and Eurasian plates, constitutes one of the world's major provinces where hydrocarbon-derived fluids have been and are still massively emitted to the earth's surface both onshore (Azerbaijan, Apennines) and offshore, particularly in the deep sea (Figure 1). In the latter case features of gas-mud expulsion lead to specific deep geological/biological environments and may strongly impact the seawater chemistry and possibly climate as well.

What are cold seeps and related features?

Cold seeps are geological features generated by emissions of fluids (of non magmatic origin) such as mud, liquids and gases and are occurring on both land and at the seafloor. Depending on their settings they are characterized by distinct morphologies.

Although cold seeps also include features such as groundwater discharge, we mainly focused during this workshop on deep-rooted emissions (several kilometres) and associated surface expressions such as mud volcanoes. As the fluids are generally hydrocarbon rich, cold seeps frequently lead to the establishment of specific and 'extreme environment' ecosystems.

Morphologic features usually related to cold seeps include carbonate mounds and carbonate crusts, pockmarks, mud volcanoes, mud domes, mud diapirs, and gas chimneys. In the marine environment, gas hydrates, and their dissociation, are believed to frequently play an important role in fluid emission.

Why study cold seeps?

Although cold seep structures have been known for a long time (since ancient Greek times!) their impact on the sea floor and environment, their mechanisms of emplacement, as well as their importance in the geological records are still poorly understood.

However, marine geological/geophysical surveys from the last decade have shown that these features are abundant and common on continental margins, where they actively participate in the shaping of continental slopes. Along continental margins cold seeps may impact the stability of submarine slopes (e.g. through the dissociation of gas hydrates) and resulting geohazards (tsunamis).

Gases emitted (mainly methane) by these features are also believed to play an important role on both regional and global carbon and fluid budgets, as well as on global climate through the expulsion of greenhouse gases.

Through microbiological activities induced by cold seeps, these also support the development of chemosynthetic ecosystems and consequently provide windows to the deep bio- and geospheres.

Finally cold seeps also provide a window to deep hydrocarbon systems both on land and onshore, which is of economic interest.

2. Overview of past research

A quick review of recent and current research on cold seeps is given along a West-East transect from the Gulf of Cadiz to the Black Sea passing through the Mediterranean Sea. A few selected examples from active and past cold seep activities occurring on land were also discussed during this workshop (see Figure 1).

Gulf of Cadiz

The Gulf of Cadiz and the W. Alboran Basin form an area of extensive hydrocarbon-rich fluid seepage, located in the tectonically active westward front of the Betic-Rifian Arc, close to the Africa/Eurasia collisional plate boundary (Henriet *et al.* and Pinheiro *et al.*, this volume). Since the recent discovery of the first mud volcanoes and gas hydrates in this area in 1999, a large number of fluid escape structures has been evidenced, which include numerous mud volcanoes (41 confirmed by coring), mud diapirs, pockmarks, carbonate mounds, large fields of methane-derived authigenic carbonate chimneys and crusts, and cold water coral communities (see Henriet *et al.*, this volume). Many of these structures are active, with extremely interesting associated ecosystems that include both chemosynthetic macrofauna and microbial consortia; the latter have had a crucial role in the precipitation of the authigenic carbonates. The extensive carbonate chimney fields are a fossil record of extensive fluid expulsion, and its dimensions, up to now, are unique in the world (see Pinhero *et al.*, this volume). The fact that the fluid escape structures in this area form a continuum from deep water (3,880 m) to the shallow continental slope/shelf and to onshore outcrops (see Hamoumi *et al.*, this volume) makes it an excellent laboratory to investigate these systems. The occurrence of large mud volcanoes, relatively close to the Moroccan shore, offers promising opportunities for observation science (long term monitoring through surface and borehole instrumentation) (see Figure 2).

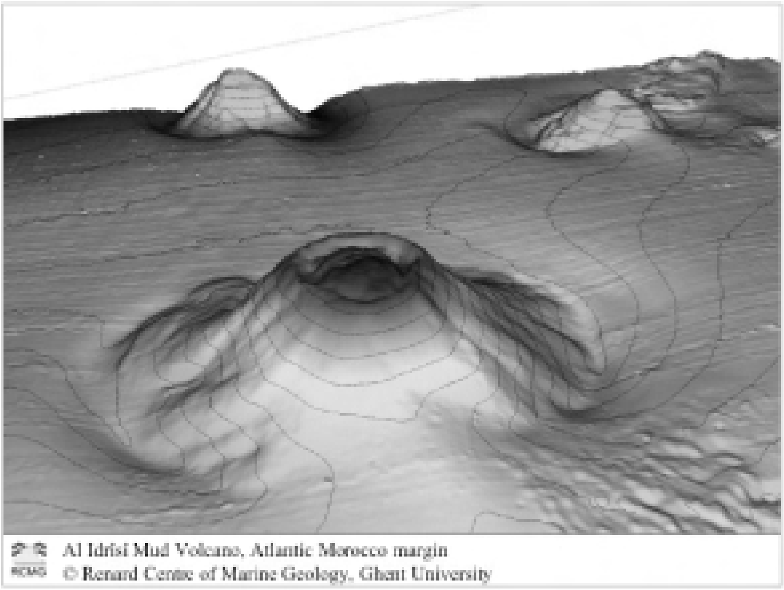

Fig.2. 3D view of Idrisi MV on the Moroccan Margin.

Calabrian Arc

The Calabrian Arc (CA) is an accretionary wedge generated by the subduction of the African plate under the European one. It is believed to be a rather young (ca. 5 Ma) and still active feature that extends (SW-NE) for about 300 km offshore the SE tip of Italy (Calabria) and connects to the Mediterranean Ridge (MR) on its NE termination.

Whereas the MR has been the focus of extensive modern geosphere and biosphere investigation during the last decades (see Huguen *et al.*, this volume) - in particular concerning cold seeps and mud volcanism - the CA remains a largely unknown geo/eco system. Nevertheless, due to its similar tectonic setting, the CA is likely to contain features (and show mechanisms) related to cold seeps and mud volcanism comparable to those already described elsewhere. Sonar data (Gloria) collected in the '60s and reinterpreted in 1981 show a few high backscatter patches indicating potential cold seeps within the backstop of the feature. In addition, high and low resolution seismic data recorded in the '70s showed features (also sampled by coring) interpreted as mud diapirs, this interpretation being supported by the compressive tectonics of the area. In order to investigate the occurrence of cold seeps and mud volcanism on the CA, a geophysical survey was carried out in summer 2005 by OGS (within the HERMES Integrated Project) (see Ceramicola *et al.*, this volume). A new province of mud volcanoes (some of them proved to be still active) has been discovered. The starting study of these features is likely to bring new insights in the driving mechanism regulating cold seeps occurrences in active continental margins, their feeding system and their relevance to geosphere-biosphere interactions.

Mediterranean Ridge

Today the Eastern Mediterranean is undergoing a complex geodynamic evolution which results from interactions between various plates, including the northwards moving Arabic and African plates now almost in collision with the SW moving Aegean-Anatolian microplate and the European plate. Along this major converging system (extending from South-West Peloponese to southern Turkey), a main morpho-structural feature is particularly prominent: the Mediterranean Ridge (MR), a large, arc-shaped, accretionary wedge, more than 1500 km long and 200-250 km wide.

As on many other active margins, a large number of mud volcanoes have been described all along the southern Aegean active plate boundary, from its Ionian junction with the Calabrian Arc (CA) up to the vicinity of the Levantine margin. Since their initial discovery (in 1981), on the seafloor of the MR south of Crete, these sedimentary features have been investigated using a large variety of tools. The distribution, morphology, backscatter characteristics, and subsurface structures of MR mud volcanoes have been described in a number of publications and several hypotheses have been put forward concerning the source, age, and emplacement of the extruded mud, the various mechanisms leading to its extrusion, and the consequences on the surrounding deep biological and geological environments.

Over the MR, more than one hundred mud volcanoes have now been identified (see Huguen *et al.*, this volume). Usually these MVs are characterized as dome-shaped morphological structures, with diameter ranging up to 10 km, but are only a few hundreds metres high (see Figure 3). On backscatter data they are often associated with large highly reflective patches indicating recently extruded mud flows. Most of the MVs are located along, or nearby, the MR backthrust area and most of these mud constructions are clearly tectonically controlled, being emplaced on structures associated to the frontal convergence between African and Aegean plates. Compression is therefore believed to be the main driving force leading to massive expulsion of overpressured mud on the seafloor. The relationship between mud constructions and transcurrent faulting is particularly well established in the western and central MR. On the central MR, *in situ* studies have indicated various degrees of activity and stages of evolution of the Mvs. Some of them are inactive, or dormant, in term of mud or fluid expulsions and are now covered by pelagic sediments. Others are associated to important brine and gas expulsions, well-developed authigenic carbonate crusts and biologic communities. For example on Napoli MV, one of the most studied MVs lying south of Crete, carbonate crusts and concretions, mainly made of aragonite or magnesian calcite (Gontharet *et al.*, this volume), show higher $\delta^{18}O$ values,

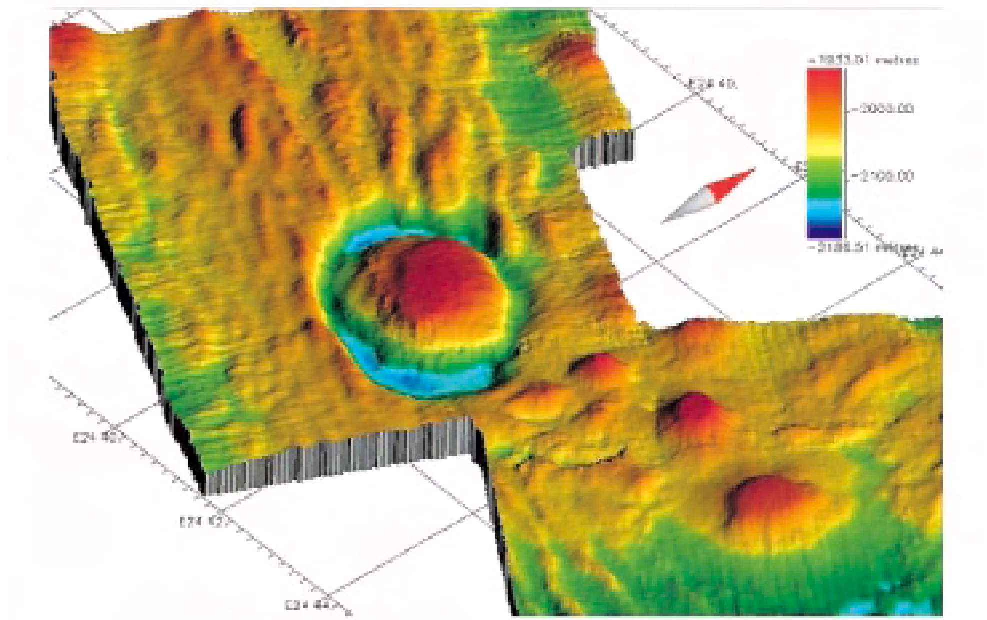

Fig.3. 3D views of Napoli and Milano MV on the Mediterranean Ridge (2,000 m water depth).

indicating a contribution of ^{18}O-rich fluids most probably originating from brines or clay dehydration (de Lange *et al*., this volume).

Anaximander Mountains

Located on important highs (Anaximander Mountains, -AM-, south west of Turkey) just to the east of the easternmost corner of the MR, the AM mud volcanoes were discovered several years ago during a survey of the R/V '*L'Atalante*' (ANAXIPROBE project). A series of further expeditions (R/V '*Gelendzhik*' 1996, R/V '*Professor Logachev*' 1999, R/V '*Pelagia*' 2003, R/V '*Aegaeo*' 2003, 2004), combined with a few submersible dives (Medinaut in 1998) documented extensive mud expulsions, methane seeping, the presence of gas hydrates and associated deep biosphere within the AM. Among the five major mud volcanoes (see Lykoussis *et al*., this volume) (Athina, Amsterdam, Kazan, Kula, and Thessaloniki), the latest four bear evidence of sub-surface gas hydrates (0.5-0.8 m below seabed). Amsterdam MV is so far the largest and the most active feature in terms of volume and extent of erupted mud breccias as well as in term of gas hydrate occurrence. Thessaloniki MV is the shallowest volcano bearing gas hydrates in the Mediterranean (1,260 m); it lies at the edge of the stability zone as determined from the depth and the seafloor temperature (~14ºC). The gas hydrates at Thessaloniki MV are thus sensitive to temperature changes and sea level fluctuations and therefore could be regarded as an ideal site for studies of MV activity, environmental impact and gas hydrate stability. According to litho-biostratigraphical analyses of mud and rock clasts (see Ioakim, this volume) two distinct palaeogeographic domains existed in the area prior to the initiation of mud volcanic activity. Mud volcanism in the eastern area (Kula, Kazan MVs) erupted clasts from the Anatolian Nape complex (Late Cretaceous limestones, Paleocene siliciclastic rocks, and Miocene mudstones and ophiolitic material) and related to the Cyprus Arc. The western province (Anaximander, Athina and Thessaloniki MVs) indicates a series of Late Cretaceous limestones, Eocene-Oligocene biogenic limestones, and Miocene mudstones which may belong to the easternmost Hellenic Arc.

Cyprus Arc

A smaller, also arc-shaped, feature, the Cyprus Arc (CyA), initiates south of Turkey (Anaximander Mountains), and includes the Florence Rise, the Cyprus margin, the Larnaka and West Taurus ridges; it finally stretches towards the Levantine coast off Syria. Over this subduction-collision related system only a few mud volcanoes have been identified up to now. In the Florence rise some MVs are likely active (or recently active) according to their backscatter signature, on the CyA most MVs appear as buried structures, only characterized by smooth morphologic conical shapes and devoid of any specific backscatter signature. On seismic data these structures show typical MV seismic signatures, such as a reflection free facies as well as, on both sides, inward dipping reflectors. On the eastern CyA, MVs are chiefly located on structural trends interfering with salt tectonics.

Nile Deep Sea Fan

The Mesozoic rifted continental margin along the southern corner of the Eastern Mediterranean includes the Nile Deep Sea Fan (NDSF) and the Levantine Margin; it is a thickly sedimented margin blanketed with total sedimentary thickness up to 12/13 km in the offshore Nile area. It is also an area of intense seepage activity discovered in 2000 (see Huguen *et al*. and Dupré *et al*., this volume). On the NDSF fluid seeping distribution is controlled by a complex interplay between deep rooted regional and shallower salt-related tectonics acting as conduits on one side, and sedimentary instabilities on the other side. A wide variety of fluid venting features have been evidenced on the NDSF seafloor: mud cones, wide caldera-like depressions, gas chimneys (up to 4 km in diameter), brine pools, pockmarks and carbonate mounds, all associated with active gas escapes, authigenic carbonate crusts (see Gontharet *et al*. and Bayon *et al*., this volume) and various chemosynthetic communities. The NDSF area has been divided into several morphostructural provinces. The western one, currently the most active domain of the deep terrigenous cone, contains tens of small-scale mud cones (a few hundred metres in diameter) and a few wide calderas (several km in diameter) all occurring at the base of the continental slope, and upper slope gas chimneys. The seafloor in the central province, submitted to numerous sedimentary instabilities and slides, is scattered by numerous pockmarks, carbonate mounds and pavements. An eastern province, bounded on its western side by a major transcurrent fault zone, is strongly controlled by salt tectonic activity. Gas chimneys, not restricted to one or the other of these provinces, delineate all along the NDSF upper continental slope a "degassing" belt.

Black Sea

Cold seeps in the Black Sea are known since ancient times as Greek authors described gas flares in the Black Sea region both on land and at sea. More recently marine exploration using multibeam bathymetry, sidescan sonar and seismic systems allowed the identification of many mud volcanoes, gas emissions and gas hydrate deposits in the entire Black Sea Basin but mostly along its margins (see Klaucke, this volume). Sedimentological and geochemical works on clasts from Black Sea MVs showed that the material and fluid composing the mud volcanoes have a common origin which is the Late Oligocene to Miocene "Maikop Formation" consisting of an up to 1,200 m thick succession of mudstones. In the absence of macrofauna in the deep anoxic basin, bacterial activity results in the formation of carbonate crusts, mainly through cementation of coccolithic carbonate oozes.

More detailed studies focusing on specific mud volcanoes determined geochemical fluxes of Li, B, CH_4 and other chemical components into the Black Sea Basin and their implication on the chemical budget of the Black Sea. Methane emissions in the Black Sea are extremely important and regional inventories of emission sites have been carried out together with budgeting the methane reservoirs at a basin-wide scale. In addition, the fate of methane in the water column has been studied in detail and the amount of methane entering the atmosphere has been quantified through both measurements and geochemical modelling.

Onshore examples

Fossil seep deposits

Studies on ancient seep/vent deposits cropping out in the Mediterranean region developed at a slower pace compared to the modern offshore seep settings (see Barbieri and Cavalazzi, this volume). Fossil seep carbonates were firstly discovered at a worldwide scale from Miocene deposits of Piedmont (Italy), and the ongoing research has been mainly concentrated on the identification of seep paleoenvironments, the geological implications, the type and amount of fluids involved, and the paleontological inventory from discrete geographic areas, such as the classical sites of the Apennines and Beauvoisin (southern France). Recent discoveries (2000) of Oligo-Miocene mud volcanoes in the Moroccan Rif belt have received geological and geochemical investigations (see Hamoumi, this volume). Whereas Mesozoic and Tertiary paleoseeps have been comparatively better investigated, Palaeozoic (even more ancient?) seeps are still at the beginning of their study. In the Mediterranean region, the best geological products of Palaeozoic cold/vent seepage occur in northern Africa (Silurian and Devonian of Morocco and possibly Algeria), and the Middle Atlas region (Morocco) hosts the oldest known (Silurian) paleoseep ecosystem. Past research on the Devonian conical mound deposits of Morocco (Hamar Laghdad and Maider basins) has focused in the stratigraphic context, some paleontological inventory and geochemical investigation (see Barbieri and Cavalazzi, this volume).

Modern onshore seepages

Surface seeps of gas, oil, and saline waters presently occur along the Adriatic side of the Apennine chain (see Capozzi and Picotti, this volume) (Figure 4). They have been considered to be indicators of deep-seated hydrocarbon accumulation and have been used, for more than 60 years, as a guide to hydrocarbon survey. A wide spectrum of seepages belongs to different geologic settings, within the uplifting chain, along the deformed foredeep on land as well as in the Adriatic Sea. The origin of these spontaneous fluid emissions has been mainly discussed on the base of the isotopic composition of gases, for exploration purpose. Recently, additional data for the reconstruction of different migration pathways of fluids have been provided by geological studies coupled with geochemical and isotopic characterization of gas, condensates and on the chemical composition of the saline waters. These studies allow understanding the first-order control played by the local geological features, which generates a very rapid spatial variation of fluids vents and variation of the geochemical characters of the seepages.

Fig.4. MV near Modena. Northern Apennines.

3. Multi reconnaissance and functioning -scale

After two days during which regional and more thematically focused presentations were made, a general discussion was organized to identify scientific questions which arise from the presence of widespread cold seep/MV phenomena (almost unknown 10 years ago) within the Mediterranean Sea and adjacent areas. The participants discussed and agreed on seven key questions and possible strategies to tentatively answer some of them.

3.1. Geological context

The control of cold seep distribution, and of their variability, by the geodynamic/geologic setting appears as the first order parameter. This parameter is the only one that is relatively well established.

Within the Mediterranean domain as a whole, cold seeps and their most spectacular morphologic expression -*Mud volcanoes*- are preferentially located on active margins and especially within the different accretionary prisms. Tectonically accreted wedges constitute obviously domains where both sedimentary loading and compressive stresses are particularly important, and where natural pathways to the seafloor are generated by ongoing tectonic activity (Gulf of Cadiz, Apennines, Calabrian Arc, Mediterranean Ridge, Anaximander Mountains, Cyprus Arc, Black Sea pro-parte). Huge sedimentary accumulations and resulting sedimentary loading represent a second typical setting for occurrence of mud volcanoes (Nile Deep Sea Fan and pro-parte Black Sea) in the Mediterranean area (Figure 4).

Many morphologic similarities exist between MV features from different geological settings (size, shape, presence of mud flow, authigenic carbonate crusts, microbial activity, etc.). Differences in the geodynamic/geological setting as well as in source rocks, in nature, volume, pressure of fluids, may however induce significant differences in the surface signatures of fluid emissions and consequently in their morphologic expressions. For example the presence of brines, gas hydrates, carbonate chimneys is not ubiquitous among the various features discussed during the workshop. More specifically, massive and thick Messinian formations in the Mediterranean Sea act as geological seals, generate specific tectonics, and have obviously played a major role in fluid seepage functioning and distribution. One of the important recommendations raised by the participants is to favor and increase comparative studies between different MV settings to better evaluate their common geological parameters. It appears also important to take advantage from onshore existing data where observations are far easier to handle, even if other environmental parameters are interfering in this specific setting.

3.2. Why cold seeps are being formed?

In order to be formed cold seeps need at first an underlying organic-matter rich source rock where thermal or microbially-induced degradation may occur. Fluids issued from this degradation will circulate into the sediments and will be stored at shallower sedimentary levels, if a necessary seal prevents them to progressively diffuse on the seabed. Such seals could be either geological seals such as for example the Messinian evaporites in the Mediterranean Sea, or secondary "physical" seals such as hydrates where important quantities of gas can be trapped. Fluids are then progressively concentrated and later discharged to the surface, if there is enough overpressure (in the case of geological seals) or adequate pressure/temperature variations (in the case of gas hydrate dissociation). This holds true if the necessary pathways such as fractures and faults exist. Among the questions to be addressed are: what are the driving mechanisms of fluid uprising? How do the feeding systems function? What are the impacts of fluid discharges on deep and shallow geo-biosphere environments?

It is fundamental to recognize and characterize the initial/deep signal (= original composition) of fluid/gas and their effect on the diagenesis.

Others crucial questions to be addressed concern the relationships between gas hydrates (formation, stability, microbiology) and gas emanation into the water column.

3.3. How are cold seeps functioning?

By analogy to lava-volcanoes, MVs are characterized by strong spatial and temporal variability. They may be explosive, eruptive, intrusive and appear to have different periodicities of (major) activity (like Stromboli compared to Vesuvius, and Napoli MV compared to Milano MV in the Eastern Mediterranean). Clearly there is no direct observation of any major MV event, but evidence is overwhelming that such events have occurred in the past and will happen again. The periodicity of activity phases clearly will have an impact not only on the amount of fluid flow but also on gas fluxes into the water column (and subsequent microbiology) and on the potential stability of gas hydrates.

We still know almost next to nothing on the duration and cyclicity of cold seeps, even though a few attempts have been made recently to sample by shallow drilling different mud flows around some MV in the Eastern Mediterranean Sea. Are fluid emissions submitted to cyclic activity? If yes, at which time scale? Do MV show intense activity phases and then are dormant before being refueled? Are small fluid emission centers such as pockmarks functioning similarly to bigger features (MV)?

The participants agree that the only way to tentatively answer some of these questions will be to develop long term basic monitoring (temperature, salinity, methane flux, etc.) in order to record direct activity signals, to assess MV variability (of moderately active MV), and to record the signal in the surrounding environment. Finally, the relationship between cold seep activity and seismicity should also be determined and eventually estimated.

3.4. Fluxes

Most of the time fluids from cold seeps are referred to as methane, carbon dioxide and hydrogen sulfide. Gases heavier than methane (ethane, propane), indicating underlying hydrocarbon systems, have been discovered locally, but the amount and variability of the different gases and other chemical compounds coming out of such features is still not known. Gas sampling is restricted to the seafloor or to shallow subsurface depths. As a consequence their composition may not be fully representative of the original composition of the gases when they formed in the source rocks.

Similarly, cold seeps are not necessary cold! Temperatures in excess of 60°C have been measured on some of the MV from the Nile margin indicating high temperature at depth. Heat flow measurements are still very scarce. Such measurements are, however, absolutely necessary to tentatively model the physical functioning of MV.

3.5. Cold seeps and gas hydrates

Some cold seeps/MVs are located in gas hydrates provinces, and gas hydrates have effectively been sampled on several of them (Gulf of Cadiz, Anaximander Mountains). In the Mediterranean Sea, the majority of MVs lies in areas where no evidence of gas hydrates has yet been found. Is the occurrence of gas hydrates only controlled by the combined effects of pressure/temperature? Why are there mud volcanoes with gas hydrates and mud volcanoes without gas hydrates?

In some areas free gas bubbles can be observed while being within the gas hydrate stability zone? Why? Is this due to gas saturation?

Is the MV activity variability related at some stage to decomposition/formation of gas hydrates?

3.6. Seeps and life

Cold seeps have a direct impact on deep sea biological environments. The degradation of gases and other chemical compounds by consortia of bacteria and archaea lead to progressive colonization by Metazoan (Figure 5). The highly contrasted Mediterranean Sea fluid seepage record may allow to answer the following open questions:

- what is the response of life (bacteria, metazoan) on fluid seepage in the full range of oceanic environments, from fully anoxic (Black Sea end term) to fully oxic (Atlantic end term) conditions?
- how does life in such environments control mineral precipitation (carbonate crusts, chimney fields) and transformation (early diagenesis in pelagic sediments and carbonate mounds)?
- what is the importance of cold seeps during the course of the Phanerozoic?
- can present day cold seeps be considered as analogues to similar associated geo/bio-processes in the past?
- is it possible to match fossil cold seep occurrences with geodynamic events?

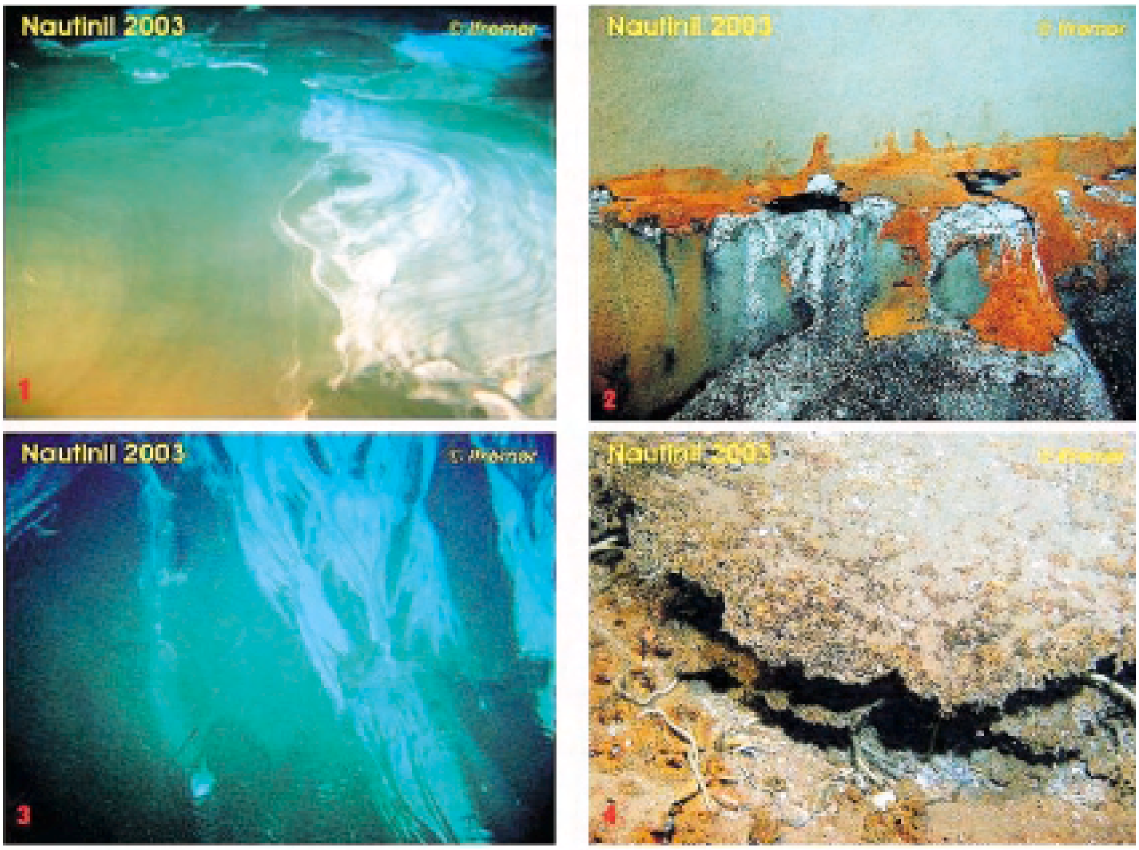

Fig. 5. Nautinil views of fluid seepages on the Nile Deep Sea Fan.
(**1**) Brine lake by 3,000 m water depth; (**2)** Bacterial aggregates on fluid seepages (3,000 m. water depth); (**3**) Bacerial filaments and flowing brines (3,000 m. water depth); (**4**) Authigenic carbonates, worm tubes and shells (2,000 m. water depth).

3.7. Cold seeps and their mineral/sedimentary environments

Understanding the processes of anoxic diagenesis in relation to different kinds of carbonate formation and their composition (including carbonate chimneys, crusts) is an important issue. Once understood the carbonate composition can be diagnostic for the processes involved.

The mineral record

Are recent seep-related mineralizations and their biological controls a key to understanding palaeoseeps, and vice-versa? (see above)

Do mineral precipitations and transformations provide us with a long-term record of fluid seepage?

The sedimentary record

Beyond the spatial extent of mud lobes and the local direct fluid-related mineralizations, can we read within the proximal pelagic sedimentary sequence a comprehensive and undisturbed record of the activity and periodicity of a fluid seepage / mud volcanic system (e.g. fall-out from explosive events and plumes)? What are the diagnostic features, the proxies that we may use to infer such processes?

4. Strategy and tools

Two types of studies are considered: (a) exploratory studies remain important issues considering for example that 10 years ago MVs were identified only onshore and partly in the Black and the Mediterranean Seas and (b) process-oriented studies are needed to understand the functioning and environmental impacts of cold seeps.

Exploratory studies

Onshore: onshore exploratory studies need to include among others remote sensing, mapping, morphostructural and stratigraphic analyses, and sedimentological studies. Particularly, the knowledge on the geotectonic/geological setting of active onshore cold seeps and MV may and should be used as guide to the search for fossil structures in similar settings of the past.

Offshore: recent experience shows that further swath bathymetry and back scattering research in standard scale in combination with other geophysical measurements is necessary before the list of the existing cold seeps occurrences in the Mediterranean and the Black Seas and the Gulf of Cadiz is completed. Deep penetration reflection-refraction seismic together with high resolution and 3D reflection seismic studies are needed to shed light to on deep seated source rocks, the possible conduits and feeding channels, as well as the detailed structure of the cold seeps and MV. High resolution micro-bathymetry, back scatter data and deep-tow vehicles are needed for a detailed image of the seep-structures and as a basis for more detailed bio-geochemical studies.

Process oriented studies

The participants of the workshop highlighted on the need for process oriented studies aiming at a better understanding of all kinds of mechanisms responsible for the formation of cold seeps phenomena. The following list of key studies may be considered as indicative and is by no means exhaustive:

- direct seafloor observations by ROVs and other specific tools may provide valuable data on the physics of active seeping and the relation between gas and brine flows;

- together with targeted short and/or long coring and subsequent laboratory analyses, they may provide insights into the largely unknown geochemical, biogeochemical and geo-microbiological processes related to the formation of, or triggered by, the cold seeps;

- novel geochemical techniques to be developed are needed to give answers;

- measurements of geotechnical properties of the mud flows are needed to better establish slope stability issues and possibly differentiate between successive flow episodes;

- the use of autoclave samplers, which will lead to the retrieval of samples under *in situ* pressure conditions, will enable the performance of innovative analyses in the laboratories;

- *in situ* measurements of temperature, salinity, and pore-pressure may shed light on the functioning of cold seeps, particularly fluxes like heat flow and fluid flow;

- the deep biosphere associated with cold seeps, the episodicity/periodicity of their activity as well as the flow stratigraphy of the MV and within the surrounding sediments need to be accessed by targeted drilling or transects of drill-holes on MVs– off MVs;

- deep fluid circulation and flow through the possible conduits may be well studied by the proper borehole instrumentation (CORK);

- last but not least, dating through improved isotopic techniques, was raised during the workshop as an absolute necessity in order to better understand the fourth dimension of cold seeps processes and the formation of structures.

Monitoring – benthic observatories

Significant variations of MV activity with time have been proven by direct observations obtained during successive cruises devoted particularly to MVs of the Mediterranean Ridge. Thus, monitoring of mud volcanoes and related processes constitutes a major task as cold seeps research evolves.

Two types of monitoring were addressed during the workshop and should be considered as a valuable technique to be included in future research initiatives: short term monitoring and long term monitoring.

In both cases among the parameters to be monitored should be micro-seismicity and its relationship with pore pressure, geochemical variations of fluids, ecosystems variability and temperature variations.

Future research efforts should focus on the deployment of benthic observatories equipped with the proper sensors which will allow the research community to monitor for the first time processes in real- or near-real time.

Modeling

Laboratory modeling may answer questions such as geological controls, episodicity, etc. Numerical modeling is however absolutely necessary to understand the physical functionning of cold seep features and particularly MVs. The temperature and geochemical properties of fluids and sediments expelled at MVs commonly differ significantly from the regional background values and therefore create anomalies of the heat flow and geochemical pore water composition. Quantifying these anomalies in time and space yields information on the nature and strength of MV activity. Numerical modeling provides a link between the different fields of observations, helps to identify the key processes that control the activity of the MV, and yields important information for planning further research. As the transfer of heat and the transport of chemical compounds in pore water are associated with different time scales, coupled geothermal and geochemical models are particularly promising for reconstructing the evolution of MVs. In addition, viscous flow models help to understand the relationship between the rheological properties of the mud and the various different topologies of MVs observed on land and on the seafloor.

5. RECOMMENDATIONS/STRATEGY

As the Mediterranean Sea cold-seeps system, from the Gulf of Cadiz over the Mediterranean Sea to the Black Sea, is by no mean exhaustively surveyed and even less understood, the need for further research towards all previously mentioned directions was stressed by all workshop participants.

Exploratory studies

Enhanced efforts should be undertaken aiming at comparing offshore cold seeps with similar structures, both active and fossil, occurring on land. Further on it is highly suggested that the present day knowledge on the geotectonic setting and the occurrence of mud volcanoes and cold seeps preferentially on the accretionary prisms of the Gulf of Cadiz, the Calabrian Arc and the Eastern Mediterranean Ridge should be applied and guide future research in order to locate similar phenomena in comparable geotectonic environments, such as the flysch deposits, of the Alpine orogenic belt around the Mediterranean Sea.

Further exploratory efforts, based on swath bathymetry, backscatter imaging and various seismic techniques at different levels of resolution, are needed in order to possibly achieve the most complete pattern of cold seeps outcrops on the seafloor of the Mediterranean Sea, including the Gulf of Cadiz and the Black Sea.

Exploratory studies should also include comparative studies of cold seeps on different geotectonic settings and try to decipher the way geodynamic processes and the presence/absence of Messinian salt control their formation, functioning and variability in activity.

Process oriented studies and monitoring

Process oriented studies should focus on specific cold seeps sites where a large data set already exists.

Active processes of fluid flow in and around mud volcanoes, including both microbial and metazoan associated ecosystems, form a straightforward target for long term observation (see also Henriet *et al*., this volume). On- and off-MV drilling transect may shed light on the temporal activity at various time-scales and may also provide evidence within the sedimentary record round them.

Process oriented studies should target among others the delineation of the initial composition of fluids and gas. As highlighted during the workshop (see also de Lange *et al*., this volume), chimneys offer a window to fluid and gas of rather initial composition compared to that at the sediment surface. Thus, actual sampling of fluid and gas at depths of a few hundreds meters below active chimneys is a real challenge, both technically and analytically.

Further on and in analogy to the Maikop Formation, which constitutes the common source rock of fluids seeping out from the Black Sea floor, efforts should be taken to identify potential source rocks in the various settings of Mediterranean Sea and Gulf of Cadiz cold seeps fields.

A fundamental target of future research should be to establish the control of different flow patterns on the morphological structure of the cold seeps. Once a cold seep is being formed, what parameters, and in which way, are responsible for the development of the one or the other cold seep structure?

The necessity of long term monitoring and the deployment of benthic observatories on key structures were already pointed out earlier. The participants agreed that beyond and in excess of any exploratory and process oriented studies, a major effort should be made to be able to monitor major parameters associated with the activity of known cold seeps.

In conclusion the workshop participants wish to stress the following principles:

- ***cold seeps need to be studied in an interdisciplinary framework;***

- ***they will provide a fertile ground for a welcome, enhanced trans-Mediterranean cooperation.***

II - WORKSHOP COMMUNICATIONS

The mud volcano province on the Atlantic Moroccan margin: towards a natural laboratory for joint European - Maghreb research.

J.P. Henriet[1], N. Hamoumi[2], M. Ivanov[3], L. Pinheiro[4], A.E. Suzyumov[5], R. Swennen[6], V. Blinova[3], I. Bouimetarhan[2], E. De Boever[6,1], D. Depreiter[1], A. Foubert[1], E. Kozlova[3], L. Maignien[7,1], J. Poort[1], P. Van Rensbergen[1] and D. Van Rooij[1]

[1] *Renard Centre of Marine Geology, Ghent University, Belgium*
[2] *Département de Géologie, Université Mohammed V-Agdal, Rabat, Morocco*
[3] *UNESCO-MSU Center for Marine Geosciences, Lomonosov Moscow State University, Russia*
[4] *Dep. Geociencias, Univ. Aveiro, Portugal*
[5] *Science Sector, UNESCO, Paris, France*
[6] *Fysico-chemische Geologie, Catholic University Leuven, Belgium*
[7] *Laboratory for Microbial Ecology and Technology, Ghent University, Belgium*

ABSTRACT

The field of giant mud volcanoes recently discovered off Larache on Morocco's Atlantic margin offers a unique setting to foster cooperative, process-oriented research of joint European and Maghreb teams. The variety of mud volcano sizes and shapes, inviting for a scrutiny of the processes controlling eruption episodicity and mud rheology, the full spectrum of associated fluid flow phenomena (bubbling seeps, chimneys, gas hydrates, carbonate crusts, carbonate mounds) and the wealth of extreme environment ecosystems, ranging from microbial communities to cold-water corals, call for a major research momentum, in coherence and pace with the large EU programmes on European margins. The shallow depth of this mud volcano province and its proximity to the shore, even suggesting a *continuum* with onshore geology, provides a unique natural laboratory and test bench for innovative sampling and long-term monitoring.

1. INTRODUCTION

For over ten centuries, the Atlantic embayment commonly referred to as the Gulf of Cadiz has acted as a major site of navigation, communication and trade between the western Maghreb and the Iberian shores, from the Sahara up to the Tagus River and even as far as Coimbra (Picard, 1997).

Long before Christians, Muslims developed a seasonal navigation which allowed Andalus people and Berbers to trade the products from the Sahara and the fertile Atlantic plains of the Maghreb for the products of craftsmanship of the Andalus cities. It is not fortuitous that the Almohades built their capitals on the western flank of their empire, in Marrakech, Rabat and Sevilla.

For over 10 million years, the Alpine orogeny has also shaped the Betic Cordillera and the Rif as one coherent geological entity, bridging Gibraltar Strait and the western Alboran Sea. The Atlantic face of this arc-shaped mountain range, born from a major but complex convergent movement of the African and Eurasian plates, has been the source of large allochtonous nappes or olistostromes which spread out over an accretionary wedge-type environment (Maldonado *et al.*, 1999; Gutscher *et al.*, 2002; Medialdea *et al.*, 2004). The expulsion of fluids has generated a swarm of large submarine mud volcanoes, first reported in the past five years (Kenyon *et al.*, 2000a; Ivanov *et al.*, 2000; Gardner, 2001; Pinheiro *et al.*, 2002; Pinheiro, this volume; Somoza *et al.*, 2003).

In the wake of these discoveries and as a major component of the grand momentum of EU projects that have driven Europe at the forefront of Margin research, tens of oceanographic cruises have circumnavigated the Gulf of Cadiz in recent years. In 2002, the Renard Centre of Marine Geology (RCMG) of Ghent University ventured to extend sub-seafloor observations, initially confined to the deeper realms of the Gulf, further upslope towards the Moroccan shelf, off Larache. The R/V *Belgica* 'CADIPOR' cruise, which had as objective to compare settings of carbonate mounds and cold water coral reefs in Porcupine Seabight off Ireland and in the Gulf of Cadiz, and the subsequent R/V *Professor Logachev* TTR 12 cruise unveiled and surveyed a most remarkable province of giant mud volcanoes: the El Arraiche mud volcano field (Van Rensbergen *et al.*, 2005) (Figure 1).

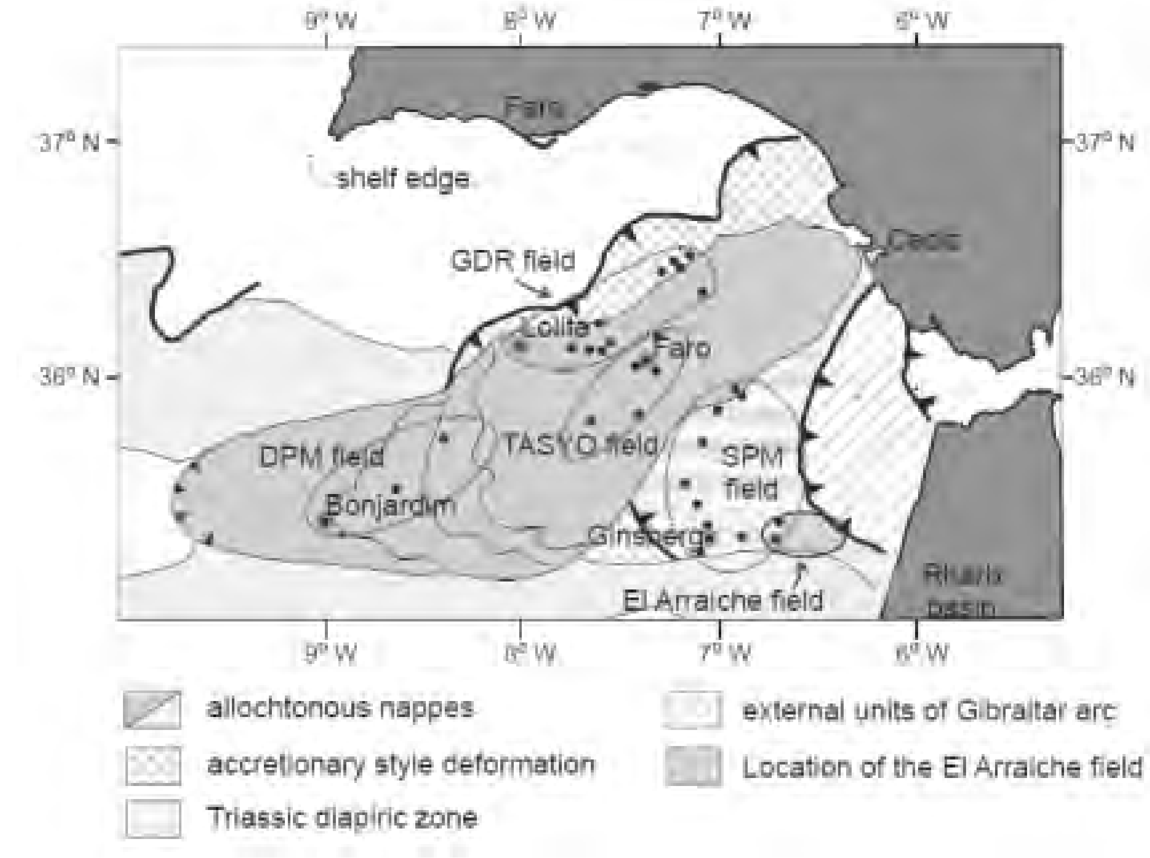

Fig. 1. Mud volcano provinces of the Gulf of Cadiz and their structural setting (Van Rensbergen *et al.*, 2005; after Maldonado *et al.*, 1999 and Somoza *et al.*, 2003). GDR: Guadalquivir ridge. DPM: deep Portuguese margin. SPM: Spanish-Moroccan margin.

Various observations argue for a most probable continuity of fluid expulsion features between the offshore mud volcano fields and onshore Morocco (Hamoumi, this volume), which opens vast perspectives of parallel and co-ordinated investigations on land and at sea. Such perspectives open a new potential field of communication and cooperation across the Gulf of Cadiz, which can confer to modern Maghreb science a deserved visibility and which can forge balanced and joint scientific and educational ventures between European and western Maghreb teams. IOC-UNESCO's recently started new programme 'Geosphere-Biosphere Coupling Processes' (GBCP) offers a frame for such a new cooperative venture. In Morocco, the universities of Rabat, Marrakech and Tangier have joined forces within the 'Morocco GBCP Consortium', in particular to actively participate in the IOC-UNESCO 'Training Through Research' Programme.

2. The El Arraiche mud volcano field

The El Arraiche mud volcano cluster (Figure 2) consists of height mud volcanoes in water depths ranging from 700 m up to the shelf edge, at a depth of 200 m. The largest mud volcano, named Al Idrissi (or Idrîsî) to honour the great geographer (1070 – 1122) (Bresc and Nef, 1999), is towering some 255 m above the seabed and is 5.4 km wide (Van Rensbergen *et al.*, 2005). The smallest mud volcanoes, named Lazarillo de Tormes and Don Quijote in honour of prominent characters from the early Iberian literature (resp. Anón. 1554 and Cervantes 1605), are only 500 m wide and 25 m high.

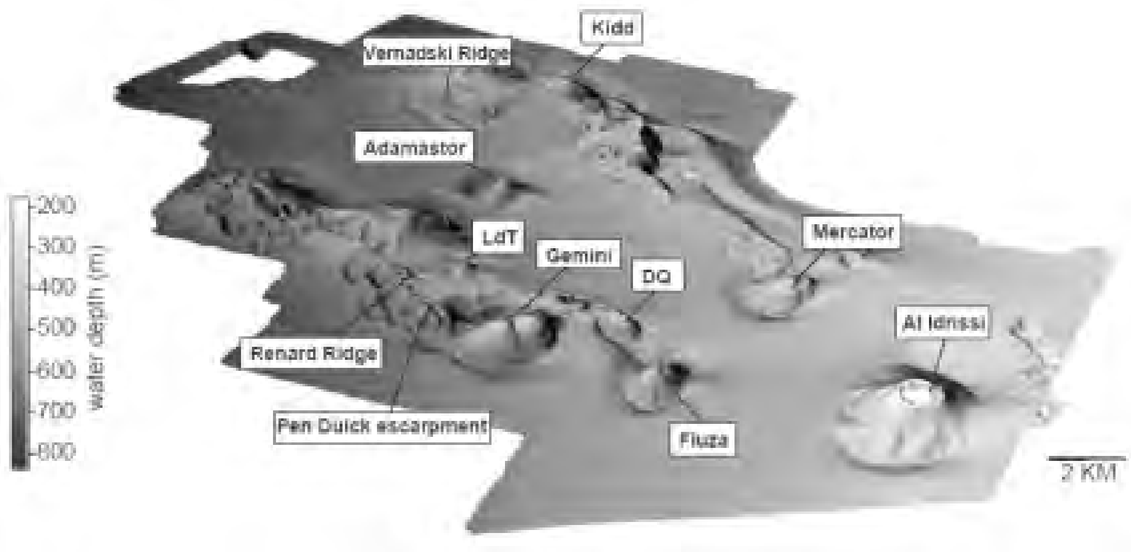

Fig. 2. Morphology of the El Arraiche mud volcano field on the Atlantic Moroccan margin, derived from multibeam bathymetry (R/V *Belgica* CADIPOR cruise) (Van Rensbergen *et al.*, 2005).

Following the discovery cruise of R/V *Belgica* and the consolidating survey of TTR 12 in 2002, a number of other cruises have set course for this most interesting sector: R/V *Sonne*, R/V *Marion-Dufresne*, R/V *Pelagia* and further cruises of both R/V *Belgica* (CADIPOR 2, 2005) and R/V *Professor Logachev* (2004-2005). Surveys up to now have included detailed multibeam bathymetry over the entire mud volcano field, dense grids of high-resolution seismic data, a few very high-resolution deep-towed chirp subbottom profiles (IFREMER), high-resolution side scan sonar images (MAK-1) over all mud volcanoes and the associated structural features, video profiles, video-guided grab sampling, gravity and piston coring, CASQ and Calypso coring and geothermal probing. A two-ship, large-offset seismic experiment of R/V *Belgica* (recording vessel) and R/V *Pelagia* (shooting vessel) in 2005 collected the first reliable seismic velocity profile. Cruises of R/V *Darwin* and R/V *Merian*, scheduled in 2006, should add high-resolution 3D seismics, ROV dives and seafloor observatories.

The El Arraiche mud volcano field is part of a larger cluster of mud volcanoes, the Spanish-Moroccan Field (Gardner, 2001) that lies within the accretionary realm but outside the main olistostrome units (Figure 1). The El Arraiche mud volcanoes line up along two conspicuous, structurally controlled ridges: the Renard Ridge, named after John Murray's co-author of the

'Report on Deep Sea Deposits' (1891, cruise of R/V *Challenger*, 1872-1876), and Vernadski Ridge, named after the author of 'Biosfera' (1926). High-resolution seismic profiles reveal that most mud volcanoes are built of a stack of lobes, interfingering with the surrounding pelagic sediments (Depreiter *et al*., 2005; Van Rensbergen *et al*., 2005). These lobes argue for an episodic activity.

One mud volcano within the El Arraiche cluster has received recent attention: the Mercator mud volcano, named after both Flanders' famous geographer (Crane, 2002) and Belgium's last sailing schoolship. Mercator mud volcano is located in water depths of 475 m and is over 125 m high. A coherent seismic reflector has been interpreted as the basis of a gas hydrate stability zone (Figure 3) (Depreiter *et al*., 2005). A stability model, using published thermogenic gas compositions from a mud volcano in deeper waters – Ginsburg mud volcano (Mazurenko *et al*., 2002) – and applied to local P-T conditions, suggests that thermogenic gas hydrates can be stable at the considered depth in Mercator mud volcano.

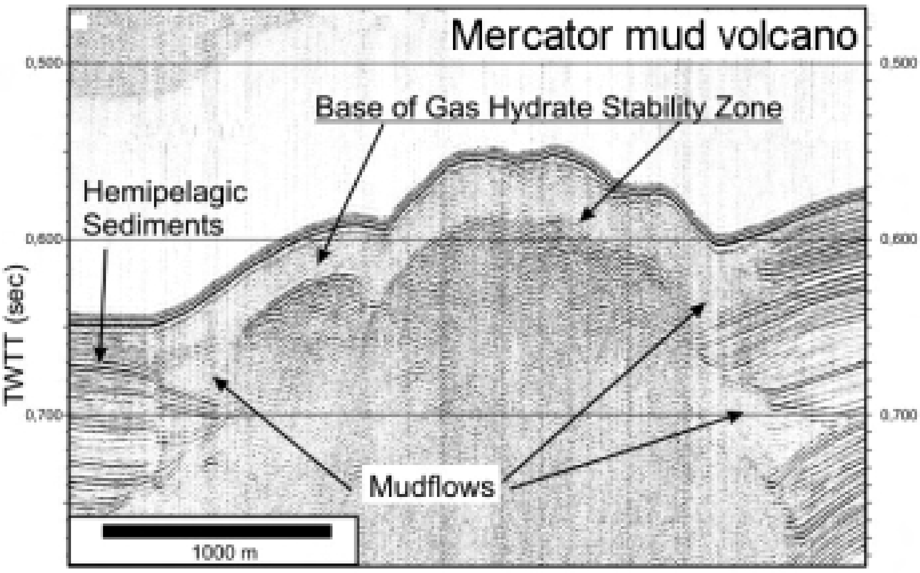

Fig. 3. Mercator mud volcano and its internal reflector, interpreted as base of the hydrate stability zone (BSR: bottom simulating reflector) (Depreiter *et al.*, 2005).

The most recent cruises of R/V *Belgica* and R/V *Professor Logachev* on the Moroccan margin have revisited Mercator mud volcano with video tracks, in particular for surveying potential drill sites within the framework of an IODP proposal. Video tracks on a flank site came across what is interpreted as a 'brown smoker', a turbid plume emanating from a small cone-shaped chimney top Van Rooij *et al*. (in press). Video tracks in the crater of Mercator mud volcano (TTR 15) unveiled bubbling methane seeps.

The potential discovery of an active seep site featuring small chimneys in 'live' position may yield a clue to the enigmatic fields of millions of small chimneys, scattered over the seabed from the Moroccan margin till the Iberian margin.

3. The Pen Duick mounds

An interesting discovery was made on Renard Ridge, where a range of small mounds is topping the Pen Duick escarpment (named after the sailing vessel of the late Eric Tabarly). Side scan sonar images and video tracks from TTR12 have shed light on the setting of the coral banks seated on large carbonate slabs or breccia-type deposits (Kenyon *et al*., 2003; Pannemans, 2003) (Figure 4). A grab sample, containing large blocks of carbonate crust associated with corals, bivalves, shell debris, etc. had a strong H_2S smell. A laboratory study of carbonate crust samples indicated that they consist of aragonite (18%), calcite (15%) and magnesium calcite (18%) with some admixture of quartz and clay minerals (Blinova, 2003). The carbon isotopic composition of the bulk carbonate samples varies from - 9‰ PDB to - 15‰ PDB, whereas separated cemented material reaches values up to - 24,2‰ PDB, showing a clear relationship with some deep source of thermogenic methane (Blinova, 2003). High-magnesium calcite-calcian dolomite cements argue for a relatively low flux and effective hydrocarbon consumption at the base of the sulfate reduction zone (De Boever, 2005).

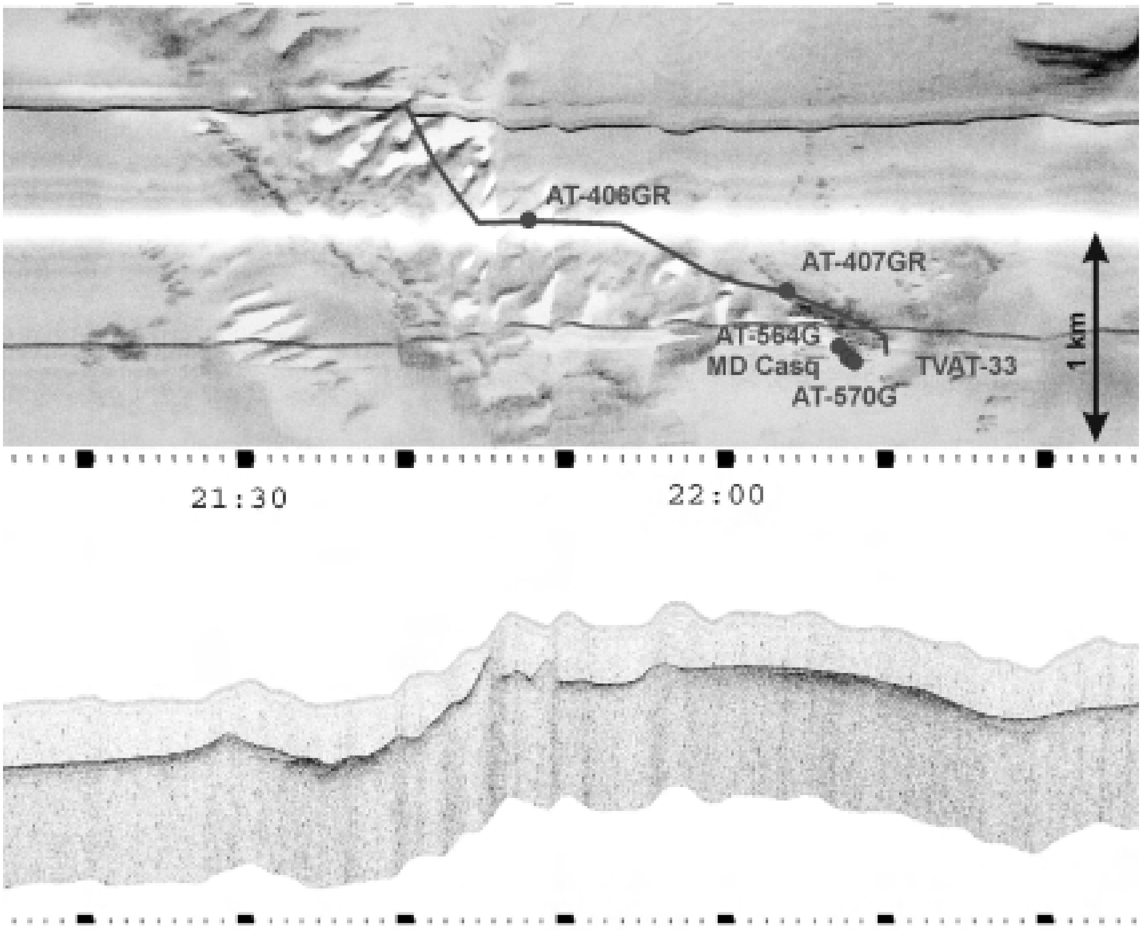

Fig. 4. Fragment of the side scan sonar (MAK-1) line across Pen Duick escarpment, with position of TV-line and sampling stations.

A process of downward growth of carbonate crusts, inferred from analytical evidence on the Nile Deep Sea Fan (Bayon, this volume; Gontharet, this volume), may possibly also be hypothesized for the Pen Duick carbonate crusts. An intriguing question deals with the fate of carbonate crusts, in particular after burial. It may be worth while to address this question by coring a transect from the off-mound regions to a mound toe, where crusts get in the initial stage of burial by the mound sediments.

In May 2004, a 9 m-long CASQ core was recovered with R/V *Marion-Dufresne* on top of one of the larger buildups – 60 m high. The core contained cold-water corals over its whole length, a striking similarity with Porcupine mound cores. A metres-thick horizon of corroded corals could consistently be traced from the Marion-Dufresne core site to a neighbouring mound, cored in 2003 by R/V *Sonne* (Foubert *et al.,* 2005). The CASQ core moreover featured a very strong smell of hydrogen sulfide. Pore water analyses gave evidence of a sharp sulfate-methane transition

(SMT) zone at 4 m below the mound top (PhD research L. Maignien); in the off-mound and distal regions, the SMT was found at greater depths (resp. 7 and 15 m). In 2005 (TTR15), the gravity core AT570G located slightly downslope the CASQ core site (Figure 4) penetrated a typical mud volcanic breccia at a depth of 175 cm bsf. A sharp increase in methane concentration was observed in the breccia.

Some relationships between carbonate mound formation and cold seepage in the Gulf of Cadiz had already been suggested some years ago (Ivanov *et al.*, 2000). However, the Pen Duick Escarpment off Morocco most probably features the most promising biogeochemically 'active' mound laboratory associated with cold-water corals, ever reported, worldwide.

4. Ocean Drilling: towards an "on mud volcano / off mud volcano" transect strategy

Various proposals have been formulated to address major scientific challenges in the Gulf of Cadiz within the **IODP** programme. Proposal 673-Pre2 'Atlantic Mound Drilling 2: Morocco Margin' for instance focuses on elucidating the processes controlling the genesis and growth of the Pen Duick mounds, within the El Arraiche mud volcano province.

An associated proposal to drill the Mercator mud volcano has been temporarily dissociated from 673-Pre, upon recommendation from IODP, but it will be developed into an independent proposal. The drilling strategy will be largely inspired by the "on mound / off mound" strategy systematically developed within the framework of mound research in Porcupine Basin and off Morocco (PhD research A. Foubert), both with Calypso coring (R/V *Marion-Dufresne*) and IODP coring (Expedition 307 on Challenger mound, Porcupine Basin W. of Ireland, Proposal 673-Pre2 off Morocco).

The rationale is that an "off mud volcano" borehole, carefully located in the proximity of a major mud volcano but beyond the reach of its mud lobes, may hold the most detailed and chronostratigraphically best constrained record of the expulsion activity and episodicity, provided that the key geochemical, sedimentological and microbiological "proxies" for mud expulsion phases can be identified and traced from the mud volcano to its direct neighbourhood.

5. Research and training prospective

The mud volcano belt in the Gulf of Cadiz is already a focus of large international research programmes. The EU **IP HERMES** (Hotspot Ecosystem Research on the Margins of European Seas) has identified the Gulf of Cadiz as a prominent target for evaluating the ecosystems associated with mud volcanoes and carbonate mounds or cold-water coral reefs. IOC-UNESCO's new programme '**Geosphere-Biosphere Coupling Processes**' (GBCP) also offers a – well tested – frame for fostering exchanges between young scientists and training at sea, in particular through IOC-UNESCO's 'Training Through Research' (TTR) programme. The 'Morocco GBCP Consortium', rallying the universities of Rabat, Marrakech and Tangier towards the objectives of GBCP studies and the training of young scientists, can hereby play a pilot role.

The active processes of fluid flow in and around the mud volcanoes of the Gulf of Cadiz and the associated ecosystems, both microbial (the Deep Biosphere and surface communities) and metazoan, also form a straightforward target for **long-term observation**, in particular in coherence with the objectives of EU FP7. A mud volcano province like the El Arraiche cluster, close to the shoreline, invites for observational science. Within the ESF EUROCORES programme, the '**Eurodiversity**' proposal 'Microsystems', in a final phase of funding negociations, proposes to develop the Pen Duick mounds into a natural laboratory for investigating microbial diversity and functionality in such mound environment.

Regional distribution and tectonic control of mud volcanoes in the Eastern Mediterranean Sea: evidence from regional swath bathymetry, backscatter records and seismic data

C. Huguen[1,7], J. Mascle[1], B. Loubrieu[2], N. Chamot-Rooke[3], L Loncke[4], J. Woodside[5], T. Zitter[6], J. Benkhelil[7] and E. Tahchi[7]

[1] *Géosciences Azur, Observatoire Océanologique, Villefranche-sur-mer, France*
[2] *DRO/GM Ifremer, Plouzané, France*
[3] *Laboratoire de Géologie, Ecole normale supérieure, Paris, France*
[4] *UPJV Faculté des Sciences, Laboratoire Sciences de la Terre, Amiens, France*
[5] *Vrije Universiteit, Amsterdam, The Netherlands*
[6] *Collège de France, Europôle de l'Arbois, Aix-en-Provence, France*
[7] *LEGEM, Université de Perpignan, Perpignan, France*

ABSTRACT

During the last ten years most of the deep basins of the Eastern Mediterranean Sea have been surveyed by swath bathymetry and back-scatter imagery. Using this set of data, we have undertaken a regional synthesis of mud volcanoes distribution, often easily detected on multibeam data as subcircular lens-shaped features and/or as high backscatter patches on the seafloor. Mud volcanoes (and related mud flows, fluid seeps and brines), are widespread in two main settings: (a) along the tectonically active Mediterranean Ridge and Cyprus Arcs which both consist of thick piles of tectonized sediments, and (b) along the Egyptian passive margin where the Nile river has constructed, since the early Pliocene, a conspicuous terrigenous wedge now covering a thickly sedimented Mesozoic passive margin segment.

Along the southern Aegean-Anatolian active boundaries, mud volcanoes, and other fluid seep related features, are distributed along a 1,500 km belt recognized all along the Mediteranean Ridge backthrust domain, from its Ionian junction with the Calabrian Arc to the south of Turkey (Anaximander mountains area), and from there extending along the Florence and Hecataeus rises (west and east of Cyprus respectively) up to the vicinity of the Levantine margin.

Less abundant, but significant mud and fluid expulsion features (sometimes associated with brines), are also detected along the Nile continental slope where they constitute either a gas chimney belt along the upper slope or appear as clusters of mud cones, chiefly at the foot of the northwestern continental slope area.

Key Words: Eastern Mediterranean, mud volcanoes, regional distribution, tectonic control.

INTRODUCTION

The Eastern Mediterranean is undergoing a complex geodynamic evolution resulting from the interaction of various plates (Mc Kenzie, 1972; Le Pichon *et al*., 1995; Mc Clusky *et al*., 2000, Mascle *et al*., 1999; 2000), including (1) the northwards moving Arabic and African plates involved in a pre-collision process with the (2) SW rotating Aegean-Anatolian microplate, itself disconnected from the (3) Eurasian plate by the North Anatolian strike-slip fault zone. Interacting with such a complex geodynamic framework, thick layers of ductile evaporites, deposited during the Messinian crisis over most of the eastern Mediterranean deep basins, trigger spectacular salt-related deformations (Gaullier *et al*., 2000; Loncke, 2002).

As a consequence of the complex tectonic framework (combining crustal and sedimentary cover deformations) and the specific sedimentary pattern (including thick layers of Messinian deposits), numerous mud/fluid expulsion structures have been emplaced in the Eastern Mediterranean.

In this paper, based on a recent compilation of multibeam and seismic data (MEDEE, PRISMED II, FANIL, BLAC, NAUTINIL and SIMED cruises), we present the different types of mud volcanoes identified over the whole Eastern Mediterranean basin (morphology, backscatter characteristics, internal structure and mud/fluid venting activity) and discuss their regional distribution, as well as emplacement hypotheses.

REGIONAL DISTRIBUTION OF MUD VOLCANOES

In the Eastern Mediterranean, mud volcanoes have been identified in two main settings (Figure 1):

- A 2000-km-long convergent system extending from southwest Peloponnesus to northwest Syria which marks the suture between the Eurasian and African plates. Along this major deformation zone, two main morphologic features are known: **(1)** The **Mediterranean Ridge**, a large, arc-shaped, accretionary wedge, more than 1,500 km long and 200-250 km wide, which results from the subduction of the African plate beneath Eastern Europe and **(2)** a second arc-shaped feature, the **Cyprus Arc**, which initiates at the level of a series of structures lying south of Turkey (Anaximander Mountains) and comprises the Florence Rise, the Cyprus margin, Larnaka and West Taurus ridges, to finally stretch towards the Levantine coast off Syria.

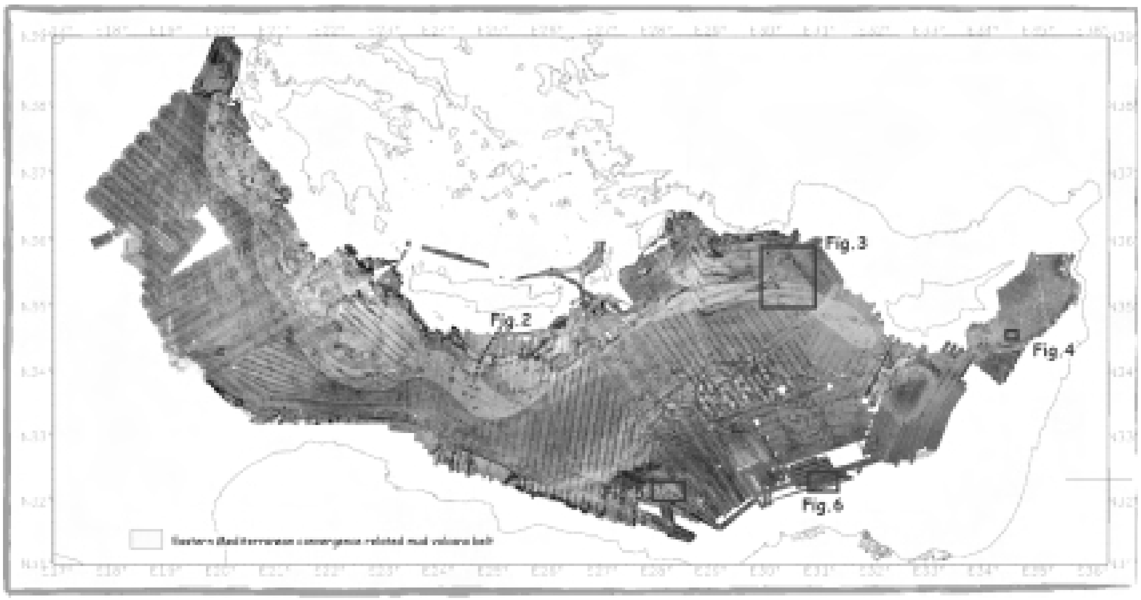

Fig. 1. Regional distribution of mud volcanoes in Eastern Mediterranean from combined backscatter data (MEDEE, PRISMED, FANIL, BLAC, NAUTINIL and SIMED cruises). Mud Volcanoes are observed over two main areas: (1) a large belt along the main convergence area (identified in light grey) and (2) a wide domain of the Nile Deep Sea Fan.

- The **Nile Deep Sea Fan**, covering the Egyptian passive margin over more than 100,000 km^2, which corresponds to a fairly thick sedimentary wedge, resulting from successive terrigenous inputs delivered by the Nile River since late Miocene.

THE NORTH MEDITERRANEAN MUD VOLCANO BELT

As on many other convergent systems, a large number of mud volcanoes are observed along the plate boundary in the Eastern Mediterranean (Limonov *et al.*, 1996). Since their first discovery on the seafloor of the Mediterranean Ridge (Cita *et al.*, 1981), these enigmatic sedimentary features have been investigated using a large variety of tools. The distribution, morphology, backscatter characteristics, and subsurface structures of mud volcanoes have been described in a number of papers and several hypotheses have been put forward concerning the source, age, and emplacement of the extruded mud, the various mechanisms leading to its extrusion, and the consequences on the surrounding deep biological and geological environments.

In this study, we try to provide an overview of all types of mud volcanoes observed along the plate boundary and focus on their location, tectonic control and potential activity, as deduced from backscatter data.

→ *Mediterranean Ridge*

Over the entire Mediterranean Ridge, mud volcanoes appear as dome-shaped reliefs with diameters ranging up to 15 km in diameter, and elevations not exceeding a few hundreds of meters (Figure 2). Most of the time these volcanoes are associated with large highly reflective patches on backscatter data, indicative of recently extruded mud flows. On seismic lines they show a typical transparent acoustic facies.

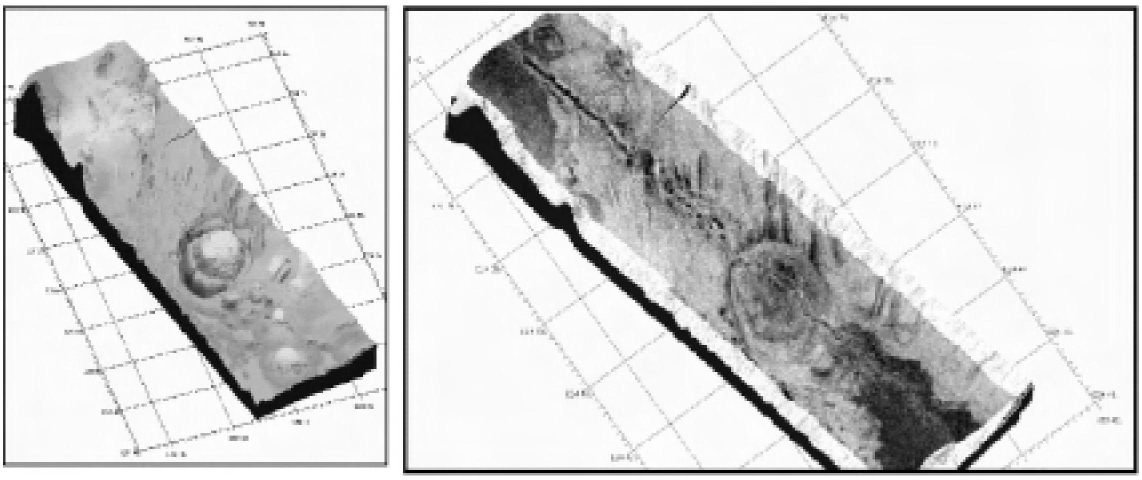

Fig. 2. 3D bathymetric view and backscatter data of the Napoli Mud volcano (Central Mediterranean Ridge; South of Crete).

The Mediterranean Ridge being now almost completely mapped with multibeam data (Figure 1), the main mud volcanoes fields have been studied in detail and appear mainly located along the backthrust area, at the boundary between the backstop and the Mediterranean Ridge Inner domain. From all studies it appears unambiguously that most of the mud constructions detected on the sea floor of the Mediterranean Ridge are tectonically controlled structures resulting from the prevailing frontal convergence between the African and Aegean plates, which remains the driving force for the mobilisation of overpressured mud. Relationships between mud expulsion phenomena and strike-slip faulting are also clearly established within the Central and Western MR (Huguen *et al.*, 2004; Chamot-Rooke *et al.*, 2005).

Finally, we can notice that highly reflective mud volcanoes are more abundant in the Western and Central RM in front of the major backstop promontories (Figure 1), in areas where the convergent stresses appear dominant, due to the south-westward motion of the Anatolian microplate.

→ *Anaximander Mountains and Florence Rise*

Within this area, located at the intersection of the Hellenic Trench and the Cyprus Arc and undergoing a complex crustal deformation, a recent study based on multibeam and deep-towed side scan sonar data (Zitter, 2004; Zitter *et al*., 2005) identified more than 30 mud volcanoes, especially over the Anaxagoras Seamount and south of Anaximenes. Most of them appear as high backscattering patches (Figure 3) associated with subcircular positive relief in the multibeam bathymetry. The largest one, Amsterdam MV, is up to 3 km across with high backscattering mud flows to the south, covering an area of more than 50 km^2.

As within the Mediterranean Ridge, clear tectonic control of mud volcano emplacement was identified within this complex area and the influence of strike-slip faults clearly demonstrated, with mud volcanoes emplaced along extensive fractures in the Anaximander Mountains and more transpressive faults along the Florence Rise.

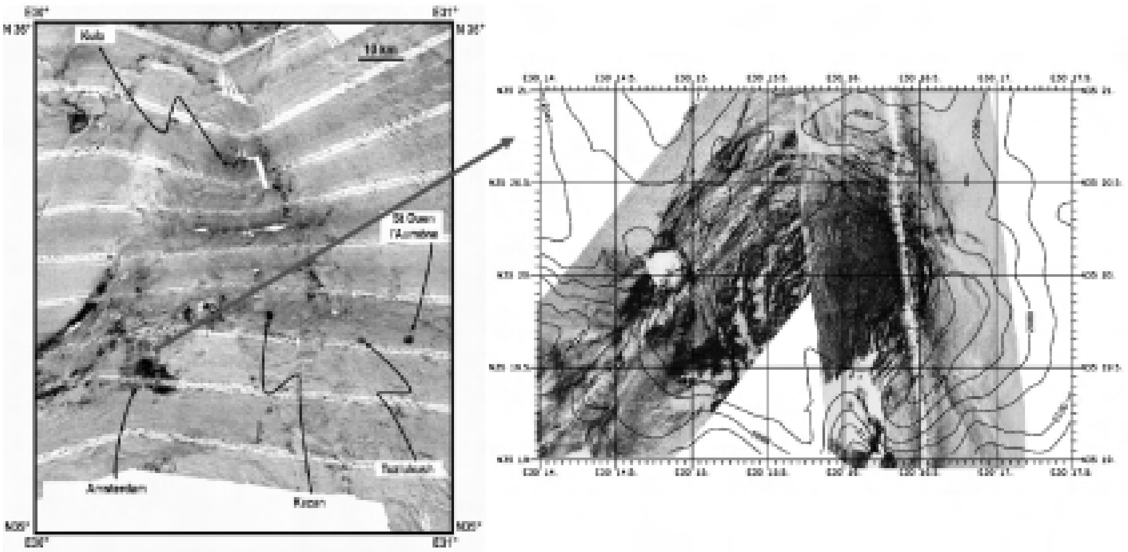

Fig. 3. Backscatter map of the Anaximander area and detail of Amsterdam mud volcano from deep-towed side scan sonar data (from Zitter *et al.*, 2005).

→ *Eastern Cyprus Arc*

Over the Eastern Cyprus Arc, only a few mud volcanoes have been identified. Most of the time, they appear as buried structures characterized by a smooth morphologic expression (Figure 4)

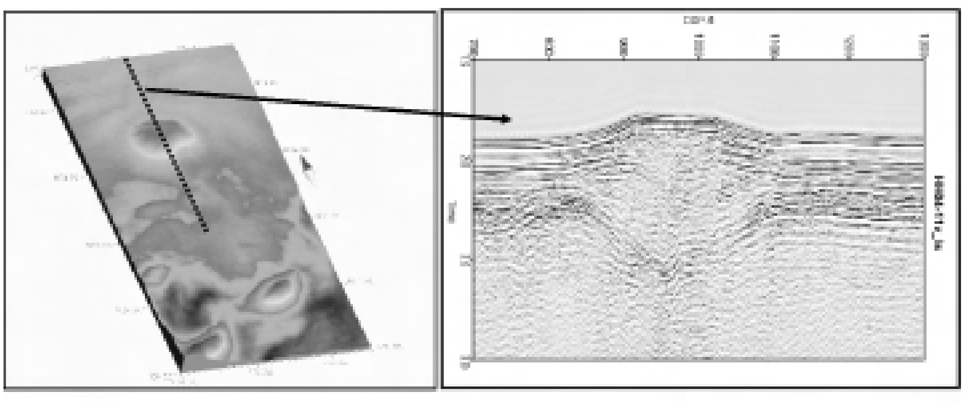

Fig. 4. 3D bathymetric view and seismic line of Barty Mud Volcano (Eastern Cyprus Arc).

and without any special backscatter signature. However, when cut by seismic lines, these structures show typical mud volcano signatures, such as a reflection free seismic facies as well as inward deeping reflectors on both sides of the structure.

A specific relationship with tectonic features is difficult to demonstrate within this area from available data, but all inferred mud volcanoes appear to be located within a lobe area with complicated hummocky and hilly topography located east of the Larnaca–Latakia domain, close to the Latakia ridge, itself a result of sinistral transpressive faulting (Ben Avraham *et al.*, 1995). A recent study (Benkhelil *et al.*, 2005) over this area indicates that the mud volcano seem to be located in an area of complex interference between salt dynamics and halokinetic processes.

The Nile Deep Sea Fan mud expulsion structures

From a recent study based on multibeam and multichannel seismic data (Loncke *et al.*, 2004), three main different types of mud/fluid expulsion structures, including mud cones, mud/gas chimneys and pockmarks, have been identified over the NDSF, according to parameters such as morphology, backscatter characteristics, internal structure and relationships with the sedimentary and tectonic frameworks. In this paper we focus on mud cones and chimneys, respectively identified within the Western and Eastern Nile Deep Sea Fan provinces.

→ *Western Province*

Within the western province, a large number of small **mud cones** with diameters ranging from 100 m to 1 km and elevations from 10 to 60 m have been observed at the foot of a growth fault system (Figure 5). These structures are generally characterized by a weak backscatter except for the summit area of some of them, where a more intense response was identified, indicating probable recent mud/fluid expulsions or the presence of diagenetic carbonate crusts. Most of these structures show typical acoustically transparent facies on the seismic data and have been identified near growth faults, rooted on the pre-Messinian layers and believed to act as preferential pathways for upward fluid migrations. The distribution of these mud/fluid expulsion features appears thus closely controlled by salt tectonics, responsible, not only for growth fault development, but also for a thinning of the sealing evaporite units and a thickening of the Plio-Quaternary sediments, both processes increasing the overpressure within deep fluid reservoirs.

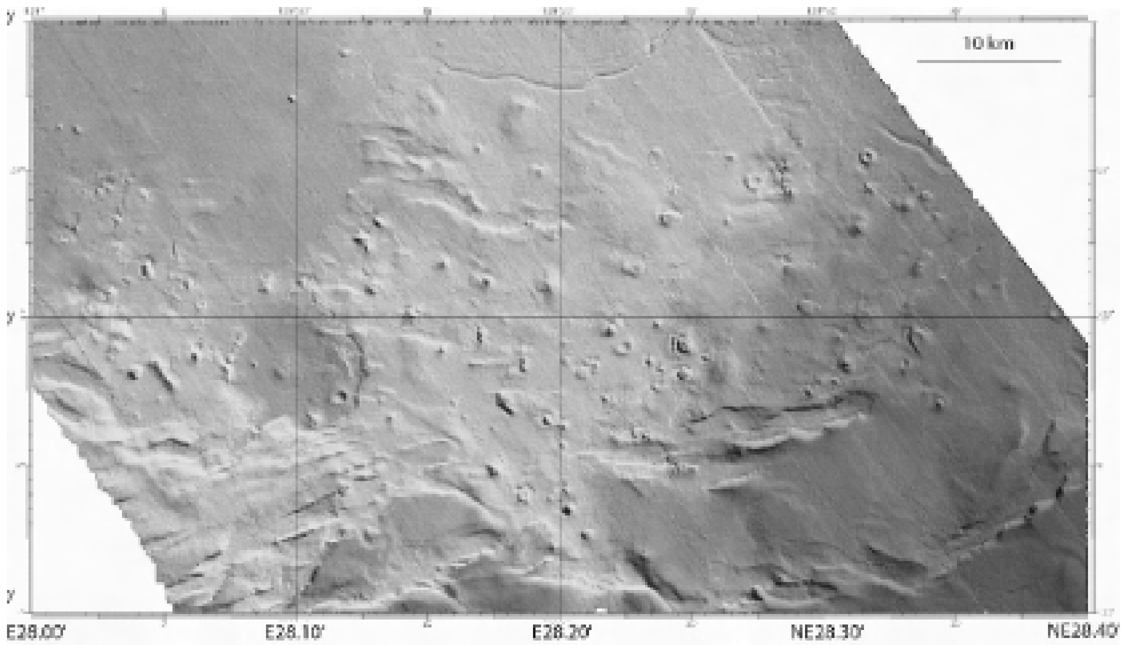

Fig. 5. Bathymetry of the Western Nile Deep Sea Fan. A large number of small mud mounds can be identified (from Loncke *et al.*, 2004).

→ *Eastern Province*

Along the NDSF upper slope, broad **gas chimneys** are observed (Figure 6), with diameters reaching 5 km, and characterized by slightly positive morphologies, often surrounded by depressed rims and displaying highly reflective centers, interpreted as the main areas for fluid/mud discharge. These structures are only observed in areas where thick Messinian salt layers have always been absent, and nearby or in connection with partly reactivated deep-rooted fault systems. On seismic data they appear as seismically transparent columnar bodies, suggesting gas-rich sediments, as confirmed by recovery of strongly degassing sediments by piston coring on top of them (Gonthier *et al.*, 2003) and recent *in situ* observations (Dupré *et al.*, this issue).

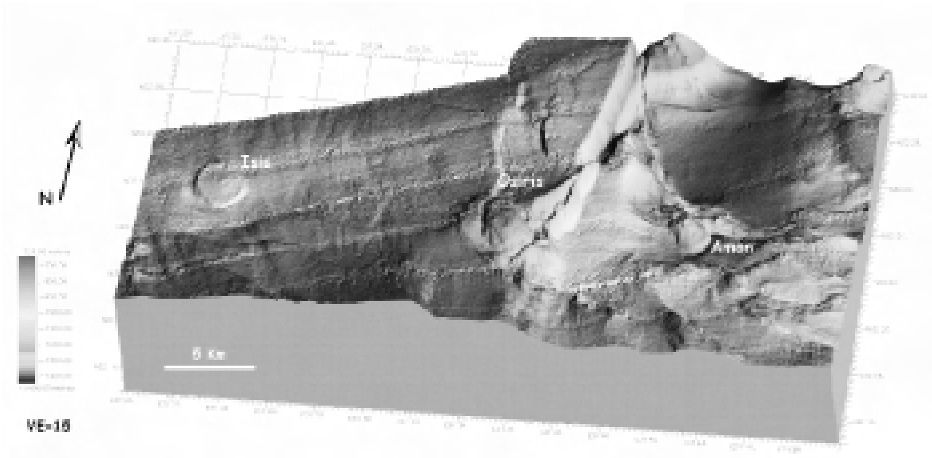

Figure 6. Large mud/gas chimneys observed within the Eastern Nile Deep Sea Fan province.

SYNTHESIS AND PRELIMINARY RESULTS

Mud expulsion related structures are identified in two different geodynamic settings in Eastern Mediterranean:

(1) A 1,500 km long and almost continuous belt is recognized all along the southern extension of the Anatolian microplate continental crust. Within this framework, mud volcanoes are observed all along the Mediterranean Ridge backthrust domain (from its Ionian corner to the Anaximander mountains area) and eastwards though Florence and Hecataeus rises (west and east of Cyprus respectively) up to the vicinity of the Levantine margin. We believe that the main driving forces for mud extrusion, within this specific plate boundary tectonic framework, are the convergence stresses between the African and Aegean plates.

(2) More scattered fields of mud mounds and chimneys are identified within the Eastern and Western Nile Deep Sea Fan. Within this passive margin framework, we believe that mud extrusions are mainly related to the important sediment overloading resulting from the continuous terrigenous input delivered by the Nile River since late Miocene.

In both domains, mud volcanoes are described as clearly connected to deep rooted faults acting as pathways for mud ascension.

(1) Within the North Mediterranean Mud volcanoes belt, relationships with strike slip faults are identified in the Western (Chamot-Rooke *et al.*, 2005), Central (Huguen *et al.*, 2004) and Eastern Mediterranean Ridge (Huguen *et al.*, 2001b) areas, as well as the Anaximander Mountains and Florence Rise (Zitter *et al.*, 2005). We believe that within this compressive plate boundary tectonic framework, strike-slip fractures provide the necessary extensional stresses to make possible the mud ascension. However, only very few largely inactive mud volcanoes are observed

in the Eastern Cyprus Arc, today controlled by a general transtensive structural framework. This brings us to the preliminary conclusion that mud volcano emplacement probably needs both a general convergent geodynamic setting (for mud and fluids overpressure) and strike-slip or normal faults (mud ascension pathways).

(2) Over the Nile Deep Sea Fan, mud volcanoes are identified either in connection with growth faults (mud mounds of the Western province) or reactivated deep-seated extensional faults (mud chimneys of the Eastern domain) (Loncke *et al*., 2004). This brings us to the conclusion that although the main driving process for mud ascension is different (sediment overloading and not compressive stresses), mud volcanoes need extensive pathways as well to reach the surface.

Finally, the absence of thick Messinian evaporites appears as one more parameter controlling the mud volcano emplacement. This is observed both for the Mediterranean Ridge, where mud volcanoes are not observed within the outer domains (built on thick Messinian levels), the Anaximander Mountains, and the Nile Deep Sea Fan, in which mud mounds or chimneys are respectively observed in connection with thinned or absent Messinian levels.

Mud Volcanoes Discovered on the Calabrian Arc: Preliminary results from the HERMES-HYDRAMED IONIO 2005 campaign.

Silvia Ceramicola[1], Daniel PRAEG[1] and the OGS Explora Scientific Party**
**** The OGS Explora Scientific Party:**
Carmine Damicantonio, Roberto De Vittor, Gaetano Di Tullio, Riccardo Codiglia, Diego Cotterle, Sebastien Garziglia (Geoscience Azur, FR), Riccardo Geletti, Maurizio Grossi, Maurizio Marchi, Caio Pelos, Isabella Tomini, Vikram Unnithan (International University Brenmen, D), Giampaolo Visnovich, Valentina Volpi, Fabrizio Zgur

[1] *Istituto Nazionale di Oceanografia e di Geofisica Sperimentale (OGS), Trieste, Italy*

In the framework of the Integrated Project HERMES (Hotspot Ecosystem Research on the Margins of European Seas) the Italian research vessel OGS Explora discovered a new province of mud volcanism in the northern Ionian Sea (Figure 1) in the summer 2005. The campaign was undertaken in cooperation with another EC (Marie Curie) project at OGS, HYDRAMED (Assessment of the Gas Hydrate System in the Mediterranean Sea). The purpose of the campaign was to investigate shallow fluid/gas escape processes on the Calabrian Arc, an accretionary prism resulting from the subduction of the African below the European plates. The Calabrian Arc was thought likely to contain cold seep features of interest to both projects, by analogy with the larger accretionary prism of the Mediterranean Ridge, which is known to contain a range of fluid escape features, e.g. pockmarks, chimneys, mud volcanoes (Camerlenghi *et al*., 1992, 1995; Mascle and Chaumillon, 1998; Kopf, 2003; Robertson *et al*., 1996c; Stride *et al*., 1997).

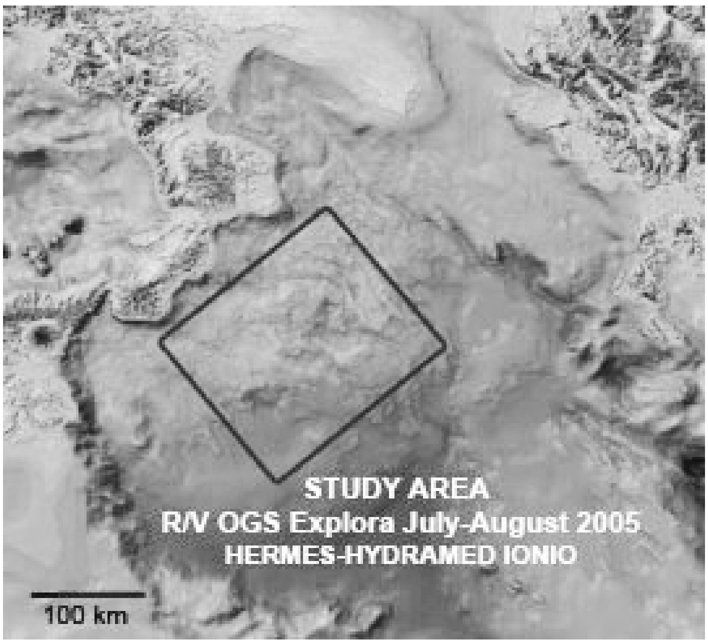

Fig. 1. Study area: the Calabrian Arc (northern Ionian Sea).

The Calabrian Arc is located offshore the toe of Italy (Figure 1) and extends for about 300 km from Sicily in the west to its intersection with the Mediterranean Ridge in the east. While the Mediterranean Ridge has been extensively investigated with modern geophysical and geological methods, the seabed morphology and shallow sedimentary cover of the Calabrian Arc received little attention since the 1980s. High-resolution sparker profiles (J lines) collected in this area in the seventies showed the occurrence of diapirs on the inner arc (Rossi and Sartori, 1981), while gravity cores acquired in 1981 (Morlotti *et al*., 1982) recovered non-marine 'chaotic' deposits, similar to volcanic mud breccias recovered from the Mediterranean Ridge but interpreted as of compressive tectonic origin. GLORIA data collected in the 1970s and re-examined by Fusi and Kenyon (1996) showed a few high backscatter patches on the Calabrian Arc, possibly indicating the occurrence of cold seeps. However, the detailed bathymetry of the Calabrian Arc remains largely unknown.

With the objective of carrying out a modern marine survey, the summer 2005 OGS campaign across the Calabrian Arc resulted in the acquisition of multibeam bathymetric data across an area of 225 x 160 km (Figure 2), as well as Chirp subbottom profiles (and gravity measurements) along 6000 km of profiles. In addition 700 km of multichannel seismic reflection data and 8 gravity cores were acquired from selected mud volcanic features. Multibeam data, covering depths from 1500 to 3500 m, revealed the large-scale tectonic structures of the inner and outer Calabrian Arc (Figure 2). Compressive and, in places, extensional tectonic structures are apparent as a complex system of enclosed depressions and highs elongate subparallel to the arc, in places including faults with clear seabed expression. The multibeam data reveal little evidence of mass failures or canyon systems, showing that the Ionian abyssal plain is not fed across the Calabrian Arc.

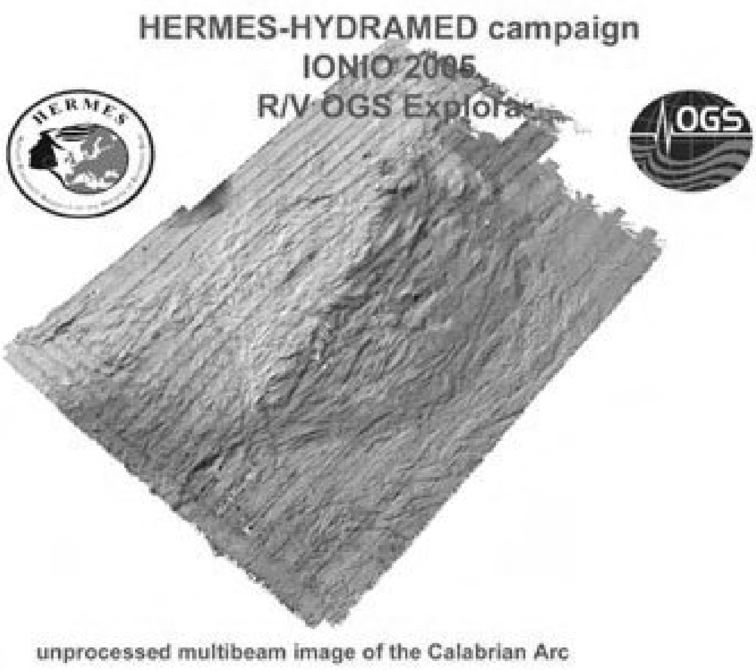

Fig. 2. Unprocessed swath bathymetric mosaic of the Calabrian.

Features of mud volcanism were identified at seabed on both the internal and the external Calabrian Arc, in water depths of 1900-2300 m (Figure 2). On the internal Arc, a pair of conical mounds referred to as the Gemelli, each up to 200 m high and 1.2 km wide, lie within an elongate seabed depression that also bounds a third circular feature of low relief to the northeast (Figure 3). Seismic data indicate the seabed depression to be structurally controlled and show the Gemelli to comprise unstratified lenses up to 300 ms thick within a Plio-Quaternary succession (Figure 4). Six gravity cores from the Gemelli proved grey mud breccias (diamicts containing angular sedimentary clasts to cobble size) to lie at or near seabed (Figure 5), suggesting recent mud volcanic activity. Gravity cores containing mud breccias were also recovered from the outer Arc, 60 km to the south, from a circular feature up to 8 km wide and 250 m high interpreted as a mud pie.

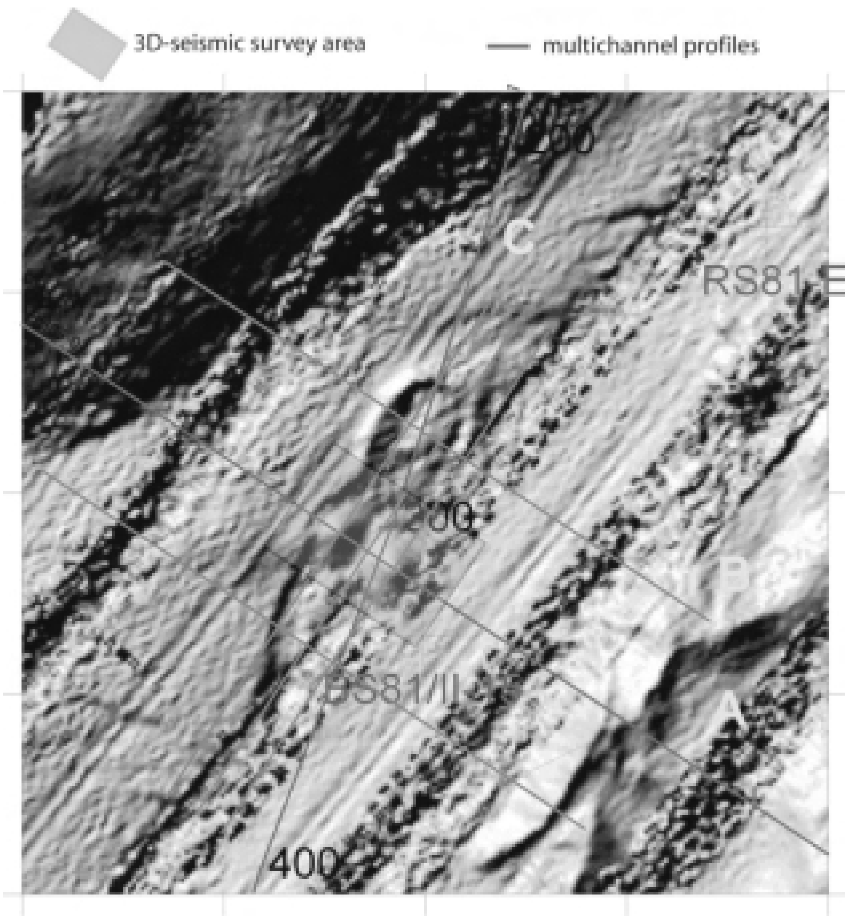

Fig. 3. The Gemelli mud volcanoes within an elongate seabed depression. The rectangle in the middle is the area of the high-resolution 3D-seismic acquisition. A, B, C are regional high-resolution profiles.

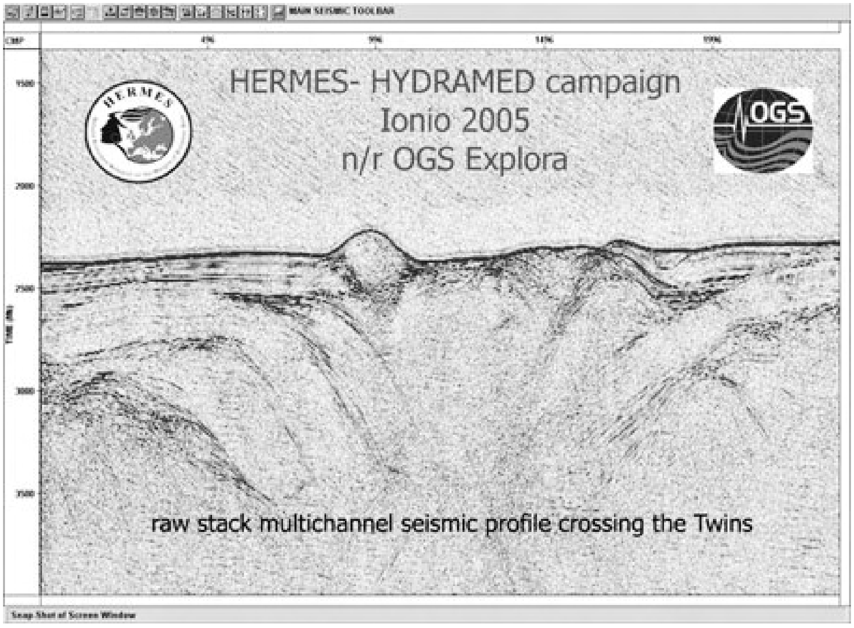

Fig. 4. Raw stack high-resolution regional line B across the Gemelli structure.

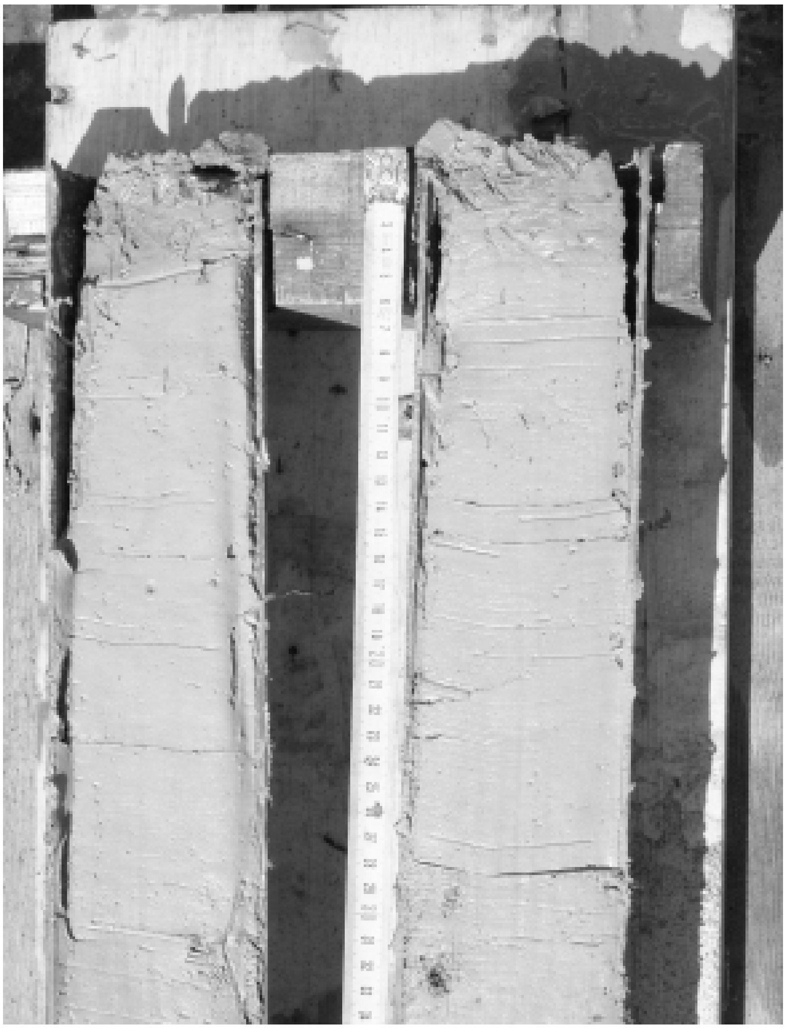

Fig. 5. Gravity core HH05-GC06.

One week of the campaign was dedicated to the acquisition of seismic reflection data across the Gemelli in order to construct a high-resolution 3D-seismic volume (Figure 3). A grid of 109 short-offset (600 m) multichannel profiles were acquired at a nominal spacing of 25 m across an area of 2.8 x 4.5 km. Over the coming months, the data will be processed into a 3D-seismic volume that will be used to examine the geometry and internal structure of the mud volcanoes and their relation to underlying structures, as well as to indicators of shallow gas and/or fluids and possible salt lenses. The coming months will also see processing of the raw multibeam data and analysis of the gravity data in order to better constrain the presence and character of fluid and gas escape features.

On board were also HERMES participants from Germany (Vikram Unnitham, IUB) and from France (Seabastien Garziglia, Geoscience Azur). The HERMES is and Integrated Project funded by the European Community 6th Framework Programme (contract GOCE-CT 2005-511234-1) and the HYDRAMED project is funded by a Marie Curie Intra-European Fellowship within the European Community 6th Framework Programme (contract MEIF-CT-2003-501814).

Mud volcanoes and gas hydrates in Anaximander Mountains (Eastern Mediterranean)

V. Lykousis[1], S. Alexandri[1] J. Woodside[2], G. de Lange[3], A. Dählmann[3], C. Perissoratis[4], Chr. Ioakim[4], D. Sakellariou[1], P. Nomikou[1], D. Casas[5], K. Kormas[6], G. Rousakis[1], D. Ballas[1] and G. Ercilla[5]

[1] *Hellenic Centre for Marine Research, Anavyssos, Greece*
[2] *Centre for Marine Earth Sciences, Free University, Amsterdam, The Netherlands*
[3] *Faculty of Geosciences, Dept. of Earth Sciences – Geochemistry, Utrecht University, Utrecht, The Netherlands*
[4] *Institute of Geology and Mineral Exploration, Athens, Greece*
[5] *Institute of Marine Sciences, Dept. Marine Geology, Barcelona, Spain*
[6] *University of Athens, Dept. of Zoology, Marine Biology, Athens, Greece*

ABSTRACT

Detailed multibeam, sedimentological, and geophysical surveys within the framework of the EU Project 'ANAXIMANDER' provided ample new data to confirm that the E. Mediterranean (Anaximander Mountains) is an important site for active mud volcanism and gas hydrate formation. More than 3000 km of multibeam track length was acquired during the two missions and 80 gravity and box cores were recovered. Major outputs: 1) Detailed bathymetry/morphology and backscatter data of the greater area compared to previous surveys; 2) Very detailed morphology of the known targeted mud volcanoes (Amsterdam, Kazan and Kula) especially the Amsterdam "crater" and the related mud breccia flows; 3) Gas hydrates were collected repetitively from a larger area of Amsterdam mud volcano at a subbottom depth of around 0.3-1.5 m; 4) Gas hydrates were sampled for the first time at Kazan MV; 5) New mud volcanoes were identified on the basis of multibeam backscatter intensity. They were sampled, documented as active and named ***"Athina"*** and ***"Thessaloniki"***. Gas hydrates were sampled also in Thessaloniki MV, the shallowest (1264 m) among all the active Mediterranean sites, at the boundary of the gas hydrate stability zone.

INTRODUCTION

Since the initial discovery of mud volcanoes in the eastern Mediterranean during the late 1970s (Cita *et al.,* 1981), mud volcanoes, mud diapirism and fluid seeps have been found in a number of different environments in the area. Most have been found on the accretionary prism of the Hellenic Arc (Mediterranean Ridge) and within the Anaximander Mountains (Woodside *et al.,* 1998); but they have also been found from offshore Sicily (Holland *et al.,* 2003) to the Nile Deep Sea Fan (Loncke, 2002; Loncke *et al.*, 2004), as well as along the Florence Rise (Zitter *et al.*, 2003) and in SE Aegean sea (Perissoratis *et al.,* 1998). International interest resulted in ODP drilling on the Napoli and Milano mud volcanoes in the Olimpi Field on the central Mediterranean Ridge in 1995 (Cita *et al.,* 1996; Robertson *et al.,* 1996a; Robertson and Kopf, 1998). To some degree the increased interest was fuelled by the inferred presence of gas hydrates based on chlorinity decrease and $\delta^{18}O$ increase in pore waters from Milano Mud Volcano (de Lange and Brumsack, 1998), whereas only a recent isotopic study showed that the fresher pore water originates from clay mineral diagenesis rather than gas hydrate dissociation (Dählmann and de Lange, 2003). However, gas hydrates were sampled in 1996 at Kula Mud Volcano in the Anaximander Mountains (Woodside *et al*., 1997, 1998). The discovery of mud volcanoes in the Anaximander Mountains was a result of a multibeam survey conducted as part of the Dutch ANAXIPROBE project in 1995 and from a follow-up survey in 1996 with seafloor sampling and deep-tow side scan imagery (Woodside *et al.,* 1997, 1998).

Following these investigations the latest European effort regarding the gas hydrate research in the Eastern Mediterranean was the EU funded project 'ANAXIMANDER' (EVK3-2001-0001233000) .

The Anaximander Mountains comprise a group of three main seamounts located between the Cyprus and Hellenic arcs (Figure 1). They are currently undergoing a neotectonic deformation characterized by strike slip faulting (Zitter *et al.,* 2003; Ten Veen *et al.,* 2004) between the westerly moving Anatolian Plate and the African Plate (McClusky *et al*., 2000). The Anaximander Mountains are described as large faulted and tilted blocks that originally were geologically continuous with south-western Turkey.

The mud volcanoes of Anaximander Mountains were unexpectedly discovered in 1995 during a detailed multibeam bathymetric survey with the swath system Simrad EM-12 of the French research vessel *L'Atalante* in the framework of the Dutch ANAXIPROBE project. In 1996, the combined expedition of the ANAXIPROBE project and the International Training Through Research programme (TTR-6), aboard the Russian research vessel R/V *Gelendzhik*, used the MAK-1 deep-tow side scan sonar, sub-bottom profiling and detailed dredging and sampling, to verify the presence of the mud volcanoes, and sampled the first gas hydrates in the Mediterranean, from the Kula Mud Volcano (Woodside *et al.,* 1997, 1998). Furthermore in 1998, the MEDINAUT programme using the submersible Nautile, deployed by the French research ship *Nadir*, performed a closer examination and took site-specific samples (MEDINAUT/ MEDINETH Shipboard Scientific Parties, 2000; Olu *et al.,* 2004; Charlou *et al.,* 2003). In 1999, cruises with the Russian R/V *Professor Logachev*, investigated mud volcanism through high-resolution side-scan sonar (O.R.E. Tech), sediment core recovering and specific measurements of

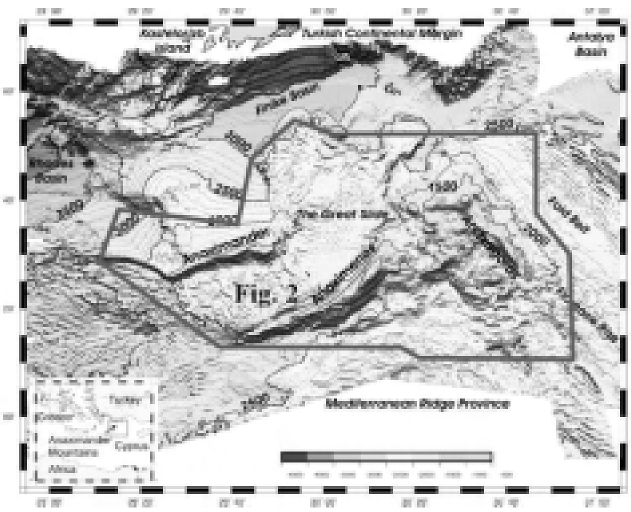

Fig. 1. Bathymetric map and major morphological features of the Anaximander Mountains and the surrounding basins acquired during the 1995 multibeam survey by R/V *L'Atalante* (Woodside *et al.,* 1997, 1998). The area enclosed by the frame was surveyed in detail by multibeam of R/V *Aegeo* during the Anaximander cruises.

methane in the water column above the mud volcanoes (MEDINAUT/ MEDINETH and SMILABLE Shipboard Scientific Parties, 2000). Several mound-like features, expressed as high reflectivity patches on EM-12D backscatter intensity maps, were examined, but only seven were proven by sampling to be mud volcanoes at that time; and two of them were identified as bearing gas hydrates – the Amsterdam and Kula mud volcanoes. Gas hydrates, first sampled from Kula mud volcano during the 1996 ANAXIPROBE/TTR-6, were sampled again at Kula during the 1999 MEDINAUT/MEDINETH expedition as well as at Amsterdam mud volcano.

DATA AND METHODS

The data presented in this study were acquired during the two cruises of the ANAXIMANDER project in the Anaximander Mountains, in May 2003 (Lykousis *et al.,* 2003) and October-November 2004.

The seafloor bathymetry/backscatter survey was carried out using a SEABEAM 2120 swath system installed on the Greek research vessel *Aegaeo* of the Hellenic Centre for Marine Research. The high resolution seismic profiling system used during the first expedition,was an analog recorder 10in^3 air gun system (PAR BOLT US). Digital data acquired, using a Delph (Triton Ellics) system.

In both expeditions, a total of 64 sediment gravity cores and 17 box-cores were recovered at "targeted" sites, selected primarily on the assessment of their backscattering intensity map.

RESULTS AND DISCUSSION

Amsterdam mud volcano

The Amsterdam mud volcano, the most prominent mud volcano in the Anaximander Mountains, is located on the southern flanks of the Anaximenes Mountain (Figure 2). It appears as a flat-topped circular-shaped mound, extending over an area of about 6 km^2, at a water depth on its summit of 2025 m. At the periphery of the mound, a ring-shaped sea-floor depression is formed, creating a relatively deep (50 m) moat northwards. Detailed morphological analysis of the Amsterdam MV indicated that there are two discrete craters the "external" and the "internal" that merge to the southeast. Both are sub circular with dimensions of 6 x 5 km and 4 x 3.3 km respectively, slightly elongated in an N-S direction. One common morphological feature is that the craters are open in the southernmost part and directly connected to the slope with a 400 m wide canyon extending down to a depth if 2250 m.

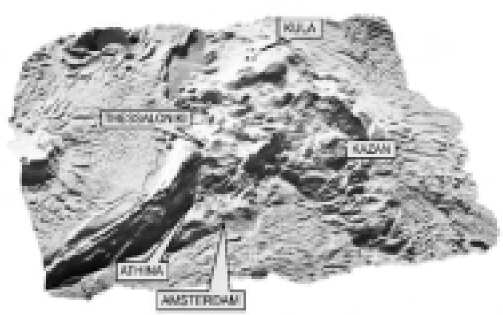

Fig. 2. Multibeam 3-D map of the Anaximander region indicating the three known (Amsterdam, Kazan, Kula) and the two newly discovered (Athina, Thessaloniki) mud volcanoes. For regional location see Figure 1.

Sediment containing gas hydrates has been sampled since 1999 at two sites, during the MEDINETH and SMILABLE cruises with R/V *Professor Logachev* and during the two cruises of R/V *Aegaeo*. During the later, seven cores containing gas hydrates from five new sites were recovered from Amsterdam MV (Figure 3).

Fig. 3. Gas hydrate lump (8 X 5 X 4 cm) (center) and broken in pieces (lower) recovered from one of the cores from Amsterdam mud volcano. Successive measurements upon recovery of sediment cores bearing gas hydrates provided minimum temperatures around 3-4 º C.

Kazan mud volcano

Kazan is an isolated hill with a hight of 50 m, lying on the edge of a relatively flat plateau of 1750 m average depth (Figure 2). The plateau lies on the southern flanks of the Eastern Anaximander Mountains, and eastwards from a major NW-SE trending fault zone separating Anaximenes from Anaxagoras SMs. It is an oval 0.6 x 0.9 km dome aligned in a N-S direction.

Gas hydrates were recovered for the first time at Kazan MV during the first cruise. Overall, during both missions, gas hydrates were sampled in 6 gravity and one box corers from four different sites on the summit. The gas hydrate crystals appeared as small rice-like lumps and were rather regularly dispersed throughout the sediment matrix deeper than about 0.3 m of core depth.

Kula mud volcano

The Kula and San Remo mud volcano cluster lies on a small triangular plateau bounded to the east and south by seamounts at the northern tip of the Anaxagoras SM range. Four mound-type edifices have been defined on the bathymetry map (Figure 2). The eastern one, closer to the Anaxagoras slope, is an irregular feature with a summit depth of 1650 m which continues northeastwards as a low elevation ridge. West of it, Kula MV is a larger circular dome-shaped mount, with a diameter of 1 km and a height of 100 m (Woodside *et al.,* 1998). Northwestwards, a cone-shaped mound of 50 m height and about 1 km in diameter corresponds to the San Remo mud volcano (Woodside *et al.,* 1997).

The sediment cores recovered from the summit of the Kula mud volcano show mud breccia to be exposed at the sea bottom only at the very top of the mud volcano.

Athina mud volcano

The newly discovered Athina MV (Lykousis *et al.,* 2004) is located at the south-eastern slope of the Anaximenes SM. The whole topography is rather complicated with steep slopes, two isolated deep basins and two mound-like topographic features along the top of the rise that separates the two basins. Both mounds display at least two distinct summits at water depths of about 1800 m, with a relative height of 10-100 m. Four sediment cores were recovered from both summits of the northward-located mound. Typical mud breccia from gravity cores on the south-western and the north-eastern summit confirmed mud volcanism and active methane seepage (Lykousis *et al.*, 2004). The core from the south-western summit (water depth 1798 m) recovered 1 m of mud breccia with a greyish matrix supporting angular-sub angular clasts of mudstone The soupy structure with high amounts of water that appeared locally in the middle of the core may be indicative of hydrate dissociation (Lykousis *et al*., 2004). The core taken from the water depth of 1783 m consisted mostly of fragments of authigenic carbonate crust, bivalves (*Lucinoma kazani)*, and worm tubes characteristic of active venting sites (Salas and Woodside, 2002).

Thessaloniki mud volcano

North-eastwards of Athina MV, at a distance of 9 km along the south-eastern slope of the Anaximenes Mountain, and at a depth of 1260 m, a small circular dome with a radius of 1.5 km, defines the Thessaloniki mud volcano. Four sediment cores were recovered from the Thessaloniki MV, all with textures of active mud volcanism (mud breccia, gas hydrate, dissociation features, etc.). From two of the sediment cores gas hydrates were collected identifying Thessaloniki as the fourth mud volcano bearing gas hydrates in the Mediterranean. Small gas hydrate lumps or flakes were dispersed in the fluidised mud. This fluidised muddy structure rich in free methane and small gas hydrate crystals was not observed previously, at least among the mud volcanoes of the European margins, indicating freshly emitted mud during a very recent activity. The unexpected discovery of gas hydrates in the Thessaloniki MV is of great importance since it is a fairly shallow MV (1260 m) and it just falls near the borders of the stability/instability zone of gas hydrate stability diagram (bottom temperature 14°C).

CONCLUSIONS

During the two recent research cruises of R/V *Aegaeo* in May 2003 and October-November 2004, the Anaximander Mountains were surveyed by sea-beam bathymetry and detailed seabed backscatter imagery, extensive sea bed sampling and (locally over mud volcanoes) by high resolution seismic profiling. The multibeam topography/imagery accurately delineated not only new morphological features of the greater Anaximander Mountains but also detailed morphological and acoustic characteristics of each individual mud volcano. The analysis of the seabed backscattering indicated potential new mud volcanoes that were confirmed by sediment gravity coring (Athina and Thessaloniki MVs). The Amsterdam mud volcano displays a well-developed almost flat-topped central dome while the Kazan, Kula, Thessaloniki and Athina MVs are rather mound-like conical mud volcanoes, probably indicating lower intensities of activity, and lower reactivation periods, narrower feeder channels, or extrusion of mud with higher shear strength, in comparison with Amsterdam mud volcano.

The large number of the sediment cores recovered enables the extension of the active mud volcanism, the delimitation of the gas hydrate field and the verification of new gas hydrate sites like the Kazan and Thessaloniki MVs. The Amsterdam MV is the most active mud volcano in the Anaximander Mountains in terms of volume and extent of erupted mud breccias and the extent of gas hydrate occurrence. A prominent characteristic is the southward moving mud flow that bears gas hydrates. This probably implies that a predominantly methane gas supply from deeper formations is located not only within the central active part, but also in the slope south of the Amsterdam MV. On the basis of systematic sampling it appears that gas hydrates occur mostly towards the central and north-eastern parts of the central dome of Amsterdam MV. Gas hydrates were also sampled, for first time, at Kazan and Thessaloniki MVs, while gas hydrate dissociation structures were found within the sediment cores from Kula and Athina MVs. Gas hydrates were observed and sampled at various depths within the sediment cores but were present usually deeper than 0.4 m from the seabed surface. The texture resembles compacted snow and the external morphology is like flakes, lumps (nodular aggregates), or big rice crystals (Kazan MV). Gas analyses on hydrate and sediment samples will be performed in order to draw a solid picture of the gas hydrate characteristics at the specific sites and will be published elsewhere (Dählmann *et al*., 2005).

The sediment cores from the Thessaloniki MV contained gas hydrates and implied recent activity. This is the shallowest mud volcano bearing gas hydrates in the Mediterranean (1260 m) at the edge of the stability zone determined by depth and seafloor temperature (~14ºC). The gas hydrates at Thessaloniki MV are thus sensitive to temperature and sea level fluctuation. Therefore this MV could be regarded as an ideal site for studies of mud volcano activity, and their environmental impact, and gas hydrate stability.

Acknowledgements

This work is a part of the EC ANAXIMANDER project (EVK-CT-2002-00068). The European Commission is acknowledged for their financial contribution to the project. The officers and the crew the R/V *Aegaeo* are gratefully acknowledged for their important and effective contribution to the field work and sampling. The Dutch Council for scientific research NWO is thanked for its support during Medineth and Smilable cruises.

Mud volcanoes and other types of cold seeps in the Black Sea: morphologies, settings and processes

I. Klaucke[1], H. Sahling[2], W. Weinrebe[1], G. Bohrmann[2] and M.K. Ivanov[3]

[1] *IFM-GEOMAR, Leibniz Institute of Marine Sciences, Kiel, Germany*
[2] *Research Centre Ocean Margins, Bremen University, Bremen, Germany*
[3] *Faculty of Geological Sciences, Moscow State University, Moscow, Russia*

ABSTRACT

Manifestations of cold fluid seepage in the Black Sea are manifold and three main types are distinguished. These include shallow water emissions of biogenic gas that are most common on passive margin settings, mud volcanoes that are most common in settings of both compressive and extensional tectonics, and deep-water seeps associated with authigenic carbonates and massive gas hydrates that are preferentially located in conjunction with thrust faulting in the eastern Black Sea.

INTRODUCTION

Cold seeps have attracted considerable interest in recent years, because emissions from cold seeps may have an influence on climate (Dimitrov, 2003), because cold seeps may add significant amounts of elements or chemical species to the oceans chemistry (Aloisi *et al*., 2004b), and because the composition of cold seep fluids provides a window to chemical processes acting at depth (Hensen *et al*., 2004). The Black Sea is particularly interesting in this respect because the Black Sea is the largest anoxic basin in the world and has only limited exchange with other oceanic basins. The deep water of the Black Sea is particularly rich in methane with high turnover rates of about 20 years (Reeburgh *et al*., 1991). As a consequence biogeochemical processes have a profound impact on the chemistry of the Black Sea, even on human timescales.

Studies of such biogeochemical processes, however, require preliminary and complementary geological and geophysical studies of the seep sites. This work includes the identification and proper localization of cold seeps, as well as detailed mapping of the seep itself and of its subsurface structures. Identification is commonly carried out with echosounding, multibeam bathymetry mapping and sidescan sonar mapping, while the deeper structures are imaged with seismic data by combining these approaches, it is possible to distinguish different types of cold seeps in the Black Sea.

COLD SEEPS IN THE BLACK SEA

Three different types of cold seeps have been identified in the Black Sea: shallow water gas emissions, submarine mud volcanoes and deep water gas seeps.

Shallow water type

Shallow water gas emissions have been identified in numerous places using shipboard echosounders on routine transits with Ukrainian research vessels (Egorov *et al*., 2003) and during subsequent work within the EU-project CRIMEA (Naudts *et al*., in press). They are obvious as acoustic anomalies (gas flares) within the water column and most of these flares are located in water depths ranging between 60 and 725 m (Naudts *et al*., in press). They are generally not associated with distinct backscatter anomalies but can be found preferentially in connection with morphologic features (pockmarks, canyon flanks, ridges and slump scars). Shallow water gas emissions are particularly abundant along the northwestern margin of the Black Sea and offshore Georgia, but this may be biased by the ships travel routes. We expect to find more gas flares in shallow all along the Black Sea margin.

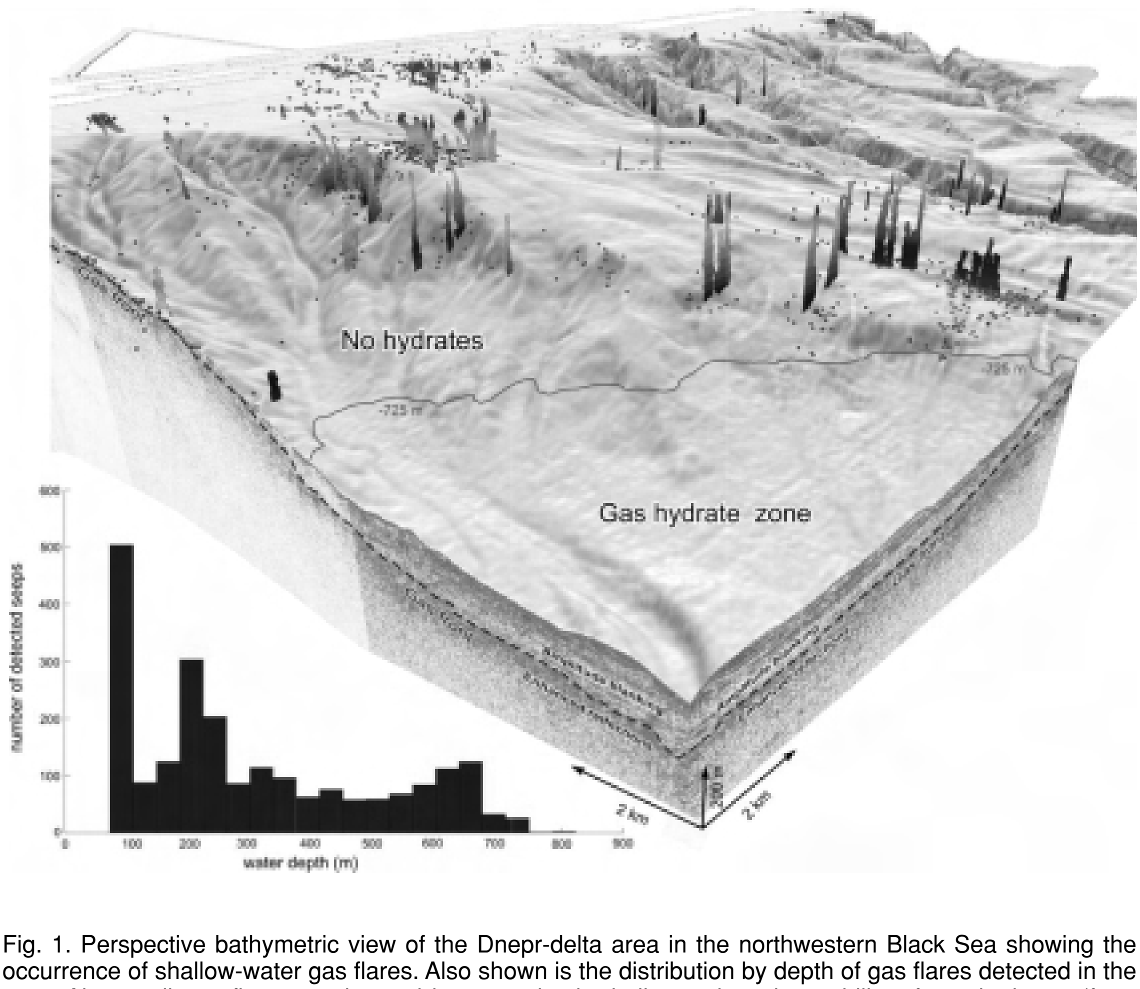

Fig. 1. Perspective bathymetric view of the Dnepr-delta area in the northwestern Black Sea showing the occurrence of shallow-water gas flares. Also shown is the distribution by depth of gas flares detected in the area. Almost all gas flares are located in water depth shallower than the stability of gas hydrates (from Naudts *et al*., in press).

Mud volcano type

Mud volcanoes are positive, rounded features that are characterised by expulsion of fluid mud and mud breccia. Many such features have been discovered in the Black Sea, mapped with multibeam bathymetry and subsequently investigated within the UNESCO Training through research (TTR) programme (Limonov *et al*., 1997). These investigations have shown that mud volcanoes in the Black Sea area are mainly composed of mud breccia originating from the Late Oligocene-Miocene Maikopian Formation. Mud volcanoes are of variable size and shape

(Figure 2); some show elevated heat flow data and gas emissions in form of gas flares (Bohrmann *et al.*, 2003). Size and shape of the mud volcanoes in the Black Sea are similar to other occurrences of mud volcanoes in the Mediterranean Sea (Huguen *et al.*, this volume; Lykousis *et al.*, this volume; Ceramicola *et al.*, this volume) and in the Gulf of Cadiz (Henriet *et al.*, this volume). The mud volcanoes have deep-rooted feeder channels, but the root itself is generally not imaged with seismic data (Krastel *et al.*, 2003). Mud volcanoes are known within a large field of the Central Black Sea, the Sorokin Trough offshore SE Crimea and isolated occurrences along the eastern and southern Black Sea margin.

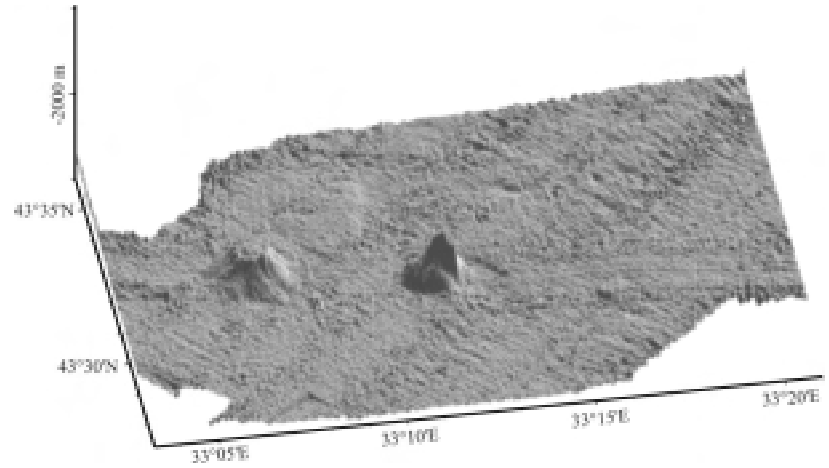

Fig. 2. 3D-bathymetric chart of two mud volcanoes in the Black Sea.

Deep-water type

Cold seeps in deep water, below 700 m water depth, are a newly recognised feature in the Black Sea. They are characterised by gas flares in the water column and high backscatter intensity on the seafloor (Figure 3). This type also shows the presence of carbonate precipitates, massive deposits of near-surface gas hydrates and in some cases oil seepage. While many of the seeps of this type show no or only very little relief, some others form 'mound'-structures similar to the mud volcano type but without indications of mud flows. To date cold seeps of this type have mainly been discovered along the eastern and southern margins of the Black Sea.

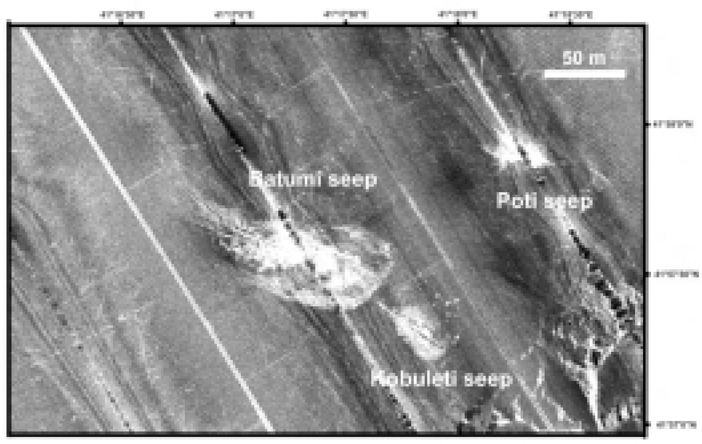

Fig. 3. High-resolution sidescan sonar image from the eastern Black Sea, offshore Georgia showing typical deep-water seeps.

CONTROLS OF COLD SEEP DISTRIBUTION

In order to gain a preliminary understanding of the factors controlling the presence and the type of cold seeps in the Black Sea, both the availability of fluids and the tectonic and geodynamic setting have to be considered (Figure 4).

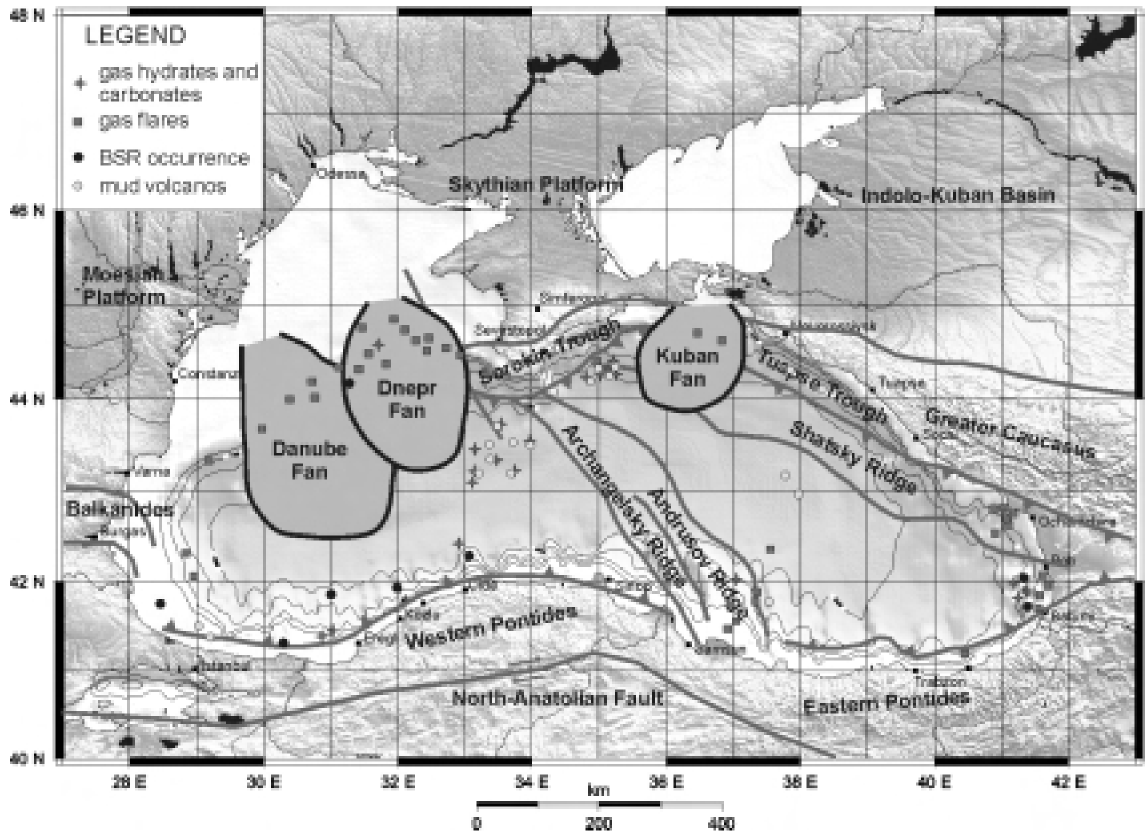

Fig. 4. Summary map of the Black Sea showing different types of cold seeps in relation to major tectonic and sedimentologic features.

Fluids and fluid availability

Different types of fluids have to be considered when studying cold seeps in the Black Sea. Most shallow water seeps emit mainly biogenic methane gas produced in the uppermost sediments by the biologically-induced oxidation of organic matter. The Black Sea sediments are particularly rich in organic matter and several sapropel layers have been identified both at the surface and in deeper layers. Mud volcanoes and deep-water seeps, on the other hand, contain a mixture of biogenic and thermogenic gas, as well as higher hydrocarbon gases. Oil seeps have also been discovered.

Geological setting

The sedimentologic, tectonic and geodynamic setting of cold seeps has a clear influence on the kind of cold seep one may encounter. Without being able at this stage to establish clear causal relationships, a link between high sedimentation rates of submarine deltaic and turbiditic depositional systems on one hand and the existence of shallow water biogenic methane seeps on the other hand can be observed. High primary productivity of the Black Sea shelf areas and rapid burial appear to favour the biogenic formation of methane, which finds abundant porous and permeable deposits where it accumulates. Along the continental slope these areas are subject to mass movements (sliding, canyon erosion) exposing these biogenic gas reservoirs at the surface.

Similarly, submarine mud volcanoes in the Black Sea appear to be related to the thickness of the underlying Maikop Formation, although the exact depth and thickness of that formation is not well constrained for the entire basin. The Maikop Formation consists of thick accumulations of clayey deposits mixed with intervals of good source rock potential and extends underneath the entire Black Sea basin. Thermal breakdown of organic matter together with differential loading of km-thick overburden leads to mud diapirism and mud volcanism.

Finally, the database of deep-water oil and gas seeps is still too limited to draw conclusions, but this type of seep appears to be related to diapirism and intense fracturing of the sedimentary succession of the Eastern Black Sea due to thrusting of the Greater Caucasus and Adjara-Trialet Fold belts. This fracturing allows hydrocarbon reservoirs at depth to leak to the seafloor.

Structural control of mud volcanism and hydrocarbon-rich fluid seepage in the Gulf of Cadiz: results from the TTR-15 and other previous cruises

L.M. Pinheiro[1,4], M. Ivanov[2], N. Kenyon[3], V. Magalhães[1,4], L. Somoza[5], J. Gardner[6], A. Kopf[7], P. Van Rensbergen[8], J.H. Monteiro[4] and the Euromargins-MVSEIS Team

[1] *Dep. Geociências e CESAM, Universidade de Aveiro, Aveiro, Portugal*
[2] *UNESCO Centre for Marine Geology and Geophysics, Moscow State University, Geology Faculty, Russia*
[3] *Challenger Division for Seafloor Processes, Southampton Oceanographic Centre, Southampton, UK*
[4] *Dep. de Geologia Marinha, INETInovação, Alfragide, Portugal*
[5] *Div. Geologia Marina, Instituto Geologico y Minero, Madrid, España*
[6] *Naval Research Laboratory, Washington DC, USA*
[7] *Research Centre for Ocean Margins, Bremen University, Germany*
[8] *Renard Centre of Marine Geology, University of Gent, Belgium*

INTRODUCTION

The Gulf of Cadiz is an area of extensive hydrocarbon-rich fluid seepage, with numerous mud volcanoes, mud diapirs, pockmarks, and several fields of methane-derived authigenic carbonates. The first mud volcanoes and gas hydrates in this area were discovered in the Moroccan sector during the TTR-9 cruise (Gardner, 2000, 2001; Kenyon *et al*., 2000a). The following year, two new mud volcano fields were discovered: the deep Portuguese field, in the South Portuguese Margin (Pinheiro *et al*., 2003a, b) and the Tasyo field, in the Spanish Sector (Somoza *et al*., 2003). Since then, the Gulf of Cadiz has been extensively investigated with 10 more cruises: TTR-10, Anastasya, TTR-11, TTR-11A, Tasyo, Cadipor, TTR-12, GAP, TTR14 and TTR-15. This included extensive geophysical coverage (single and multi-channel reflection seismics, deep-towed high-resolution seismic profiling, long-range and high resolution side-scan sonar (12, 30 and 100 kHz) and heat-flow measurements), underwater video observations, and sampling with TV-controlled grab, dredges and gravity cores. A large number of fluid escape structures have been identified and 34 of these have been confirmed by coring to be mud volcanoes. Several mud cones (e.g., Lolita, Ibérico, Tarsis) and elongated diapiric ridges (e.g., Guadalquivir, Cadiz, Formosa, Vernadsky, Renard) were also found. The mud volcanoes are located at water depths ranging from ca. 200 m to over 3880 m. Gas hydrates have, until present, been recovered from three mud volcanoes (Bonjardim, Captain Arutyunov and Ginsburg) but there are indications that these may also exist in other structures (e.g., Carlos Ribeiro). The composition of the gases from the gas hydrates indicates a thermogenic origin that suggests the possible existence of oil basins at depth. Authigenic carbonate crusts and chimneys were also discovered in the northern part of the Gulf of Cadiz, near the main channel of the Mediterranean Outflow (MOW), in 2000 (Diaz-del-Rio *et al*., 2003). These are now known to occur in various other areas of the Gulf of Cadiz, particularly along diapiric ridges at or near the main channel of the MOW. Geochemical and geomicrobiological studies have shown that they are methane-related and formed through microbial mediation. In August 2005, during the TTR-15 Leg 4, jointly funded by the *MVSEIS* Euromargins Project (PDCTM/2003/DIV/ 40018/99), the *HERMES* EU Integrated Project (GOCE-CT-2005-511234), the Belgian Research Program *TTR-Africa*, and the IOC of UNESCO, three new mud volcanoes (Porto, Soloviev and Semenovich) were discovered in the deep Portuguese field. One new area of carbonate chimneys was also discovered in the northern sector of the Gulf of Cadiz and evidence of local active gas bubbling was found for the first time on the Mercator mud volcano, in the Moroccan Margin, close to an area where emanation of fluids had been previously reported (Jean Pierre Henriet, pers. comm.).

GEOLOGICAL SETTING

The Gulf of Cadiz is located at the westward front of the Betic-Rifian Arc, in the easternmost sector of the Azores-Gibraltar segment of the Africa/Eurasia collisional plate boundary. This area is tectonically active, with a stress pattern characterized by a combination of important strike-slip movement (along the Azores-Gibraltar fracture zone) and compressional tectonics related to the Africa-Eurasia NW-directed convergence since the Cenozoic (Ribeiro *et al*., 1996). Presently, the direction of maximum horizontal compressive stress along this segment of the plate boundary is estimated to be approximately WNW-ESE in the Gulf of Cadiz, leading to a general transpressive regime in this area (Cavazza *et al*., 2004). This area has a very complex geological history with several episodes of rifting, compression and strike-slip motion since the Triassic (Dewey *et al*., 1989; Maldonado *et al*., 1999). The westward migration of the Alboran domain during the Miocene caused the Gulf of Cadiz to behave as a forearc basin associated with the formation of the Betic-Rifian Arc (Bonnin *et al*., 1975; Auzende *et al*., 1981; Maldonado and Comas, 1992; Lonergan and White, 1997; Maldonado *et al*., 1999). This phenomenon was related to the post-Oligocene extensional regime in the western Mediterranean and the formation of the neogene back-arc basins (Lonergan and White, 1997; Rosenbaum *et al*., 2002). During the final stages of the accretion of the Betic-Rifian Arc and the emplacement of the thrust units, during the Tortonian, gravitational sliding of mobile shale and salt stocks formed a giant complex of mass-wasting deposits, generally known as the *Gibraltar Olistostrome*, that reached as far west as the Horseshoe and Seine abyssal plains. This feature appears as a chaotic, highly diffractive body, with high-amplitude reflections on the seismic sections and consists of a mixture of Triassic, Cretaceous, Paleogene and Neogene sedimentary units, overlying a Palaeozoic basement (Maldonado *et al*., 1999). It involves a huge volume of mud and salt diapirism associated with Triassic salt units and undercompacted Early-Middle Miocene plastic marls (Maldonado *et al*., 1999). The origin of this chaotic body is controversial. Several interpretations have been proposed: (1) a complex of olistostromes and debris flows, originated by gravitational sliding, and tectonic thrusted units - tectonic *mélanges* (Torelli *et al*., 1997; Maldonado *et al*., 1999; Medialdea *et al*., 2004); (2) an accretionary complex related with the migration of the Alboran terrain as a consequence of a once active subduction zone (Royden, 1993; Lonergan and White, 1997; Rosenbaum *et al*., 2002); (3) an accretionary wedge associated with an active subduction beneath Gibraltar, which would explain the active mud volcanism associated with the accretionary wedge (Gutscher *et al*., 2002).

MUD VOLCANOES, MUD DIAPIRS AND DIAPIRIC RIDGES

The available side-scan sonar images from the Gulf of Cadiz show a large number of high-backscatter, approximately circular features throughout the area, that probably correspond to mud volcanoes/diapirs, pockmarks or other structures related to fluid seepage. Until present, 34 such structures have been investigated with geophysical methods and shown, by coring, to be mud volcanoes (Figure 1). These mud volcanoes are approximately conical features, located at water depths between 200 and 3880 m (top of the mud volcanoes). Their diameter can reach 5 km and their height can attain over two hundred meters. The largest mud volcanoes (e.g., Al Idrissi, Yuma, Ginsburg) are located in the Moroccan Sector (Gardner, 2000, 2001; Kenyon *et al*., 2001, 2002a; Pinheiro *et al*., 2003a,b; Somoza *et al*., 2001, 2002, 2003; Van Rensbergen *et al*., 2005a; Depreiter *et al*., 2005; Henriet *et al*., this volume), whereas the deepest are located in the S. Portuguese margin (Bonjardim, Olenin, Carlos Ribeiro, Porto, Semenovich and Soloviev). The combined interpretation of side-scan sonar mosaics (both 12 and 30 kHz) and seismic profiles (both high resolution, conventional and deep multi-channel seismic data) suggest that many of these structures appear to be aligned along major conjugate NE-SW and NW-SE trending faults, or located at fault intersections.

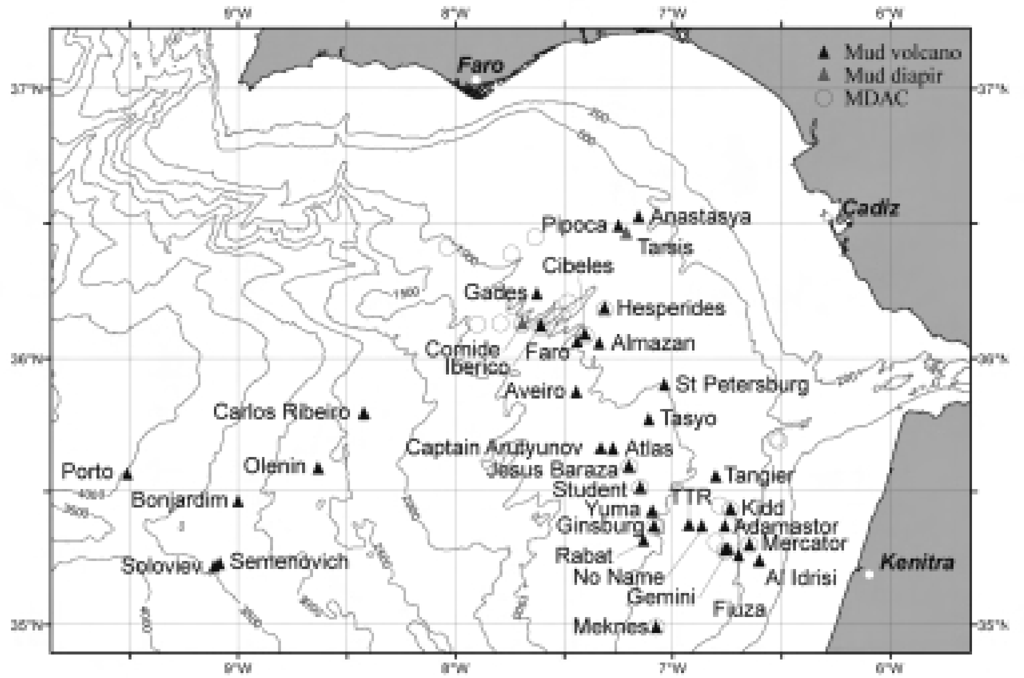

Fig. 1. Location of the mud volcanoes (black triangles), mud cones/diapirs (grey triangles) and methane-derived authigenic carbonates MDAC (open circles) discovered in the Gulf of Cadiz, since 1999 (Gardner, 2000, 2001; Pinheiro *et al.*, 2003; Somoza *et al.*, 2003; Van Rensbergen *et al.*, 2005a; Depreiter *et al.*, 2005; Henriet *et al.,* this volume).

Many of these mud volcanoes appear to have been recently active, given the fact that near-surface gas hydrate can be found, together with a high saturation in H_2S and hydrocarbon gases (mainly methane) in the mud breccia and overlying pelagic sediments. Also, chemosynthetic fauna (including Pogonophoran worms) has been observed in many of the cores, grabs and video profiles (Pinheiro *et al*., 2003).

Most of the cores retrieved from the mud volcanoes consist of a highly gas-rich mud breccia, with clasts of various lithologies and a strong H_2S smell. In the structures that have not been active recently, the mud breccia is sometimes covered by a thin layer of hemipelagic sediment. The study of the mud breccia clasts is very important because they can reveal the age and lithology of the underlying formations, which have been crossed by the rising gas-charged mud at a high pressure, probably along faults. Micropaleontological studies revealed that the older clasts are from the Upper Cretaceous, although the majority of the clasts are of Eocene and Miocene-Pliocene age (Sadekov and Ovsyannikov, 2000).

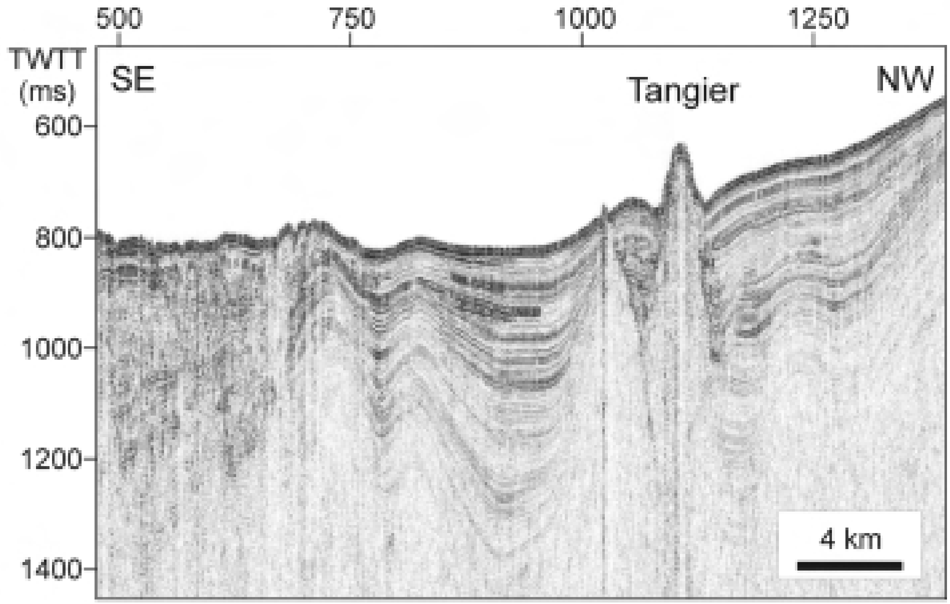

Fig. 2. Seismic profile PSAT-121. This SE-NW seismic line, shot in the Moroccan sector of the Gulf of Cadiz, crosses the Tangier mud volcano, as well as four other smaller structures (possibly also mud volcanoes) to the SE (near shotpoints 700 and 1010). The structural control of the mud volcanoes along major thrusts and faults is clear on this image.

METHANE-DERIVED AUTHIGENIC CARBONATE CRUSTS AND CHIMNEYS

Methane-derived authigenic carbonates (MDAC) from the Gulf of Cadiz (Diaz-del-Rio *et al.*, 2003) show a large variety of shapes and mineralogy. Based on their macroscopic, morphological and textural characteristics, two main different types of MDAC have been defined: (1) crusts, nodules and chimneys, where dolomite and high Mg-calcite are dominant; (2) pavements or carbonate build-ups, where aragonite is dominant. Underwater video profiles together with side-scan sonar images and seismic data suggest that the MDAC, particularly the dolomite-dominated, often occur along diapiric ridges associated with either deep-rooted strike-slip faults (mainly NE-SW, but also the conjugate NW-SE set), or with mud volcanoes/diapirs that appear to be located either along these faults or at their intersection with the arcuate thrusts from the Gibraltar Arc. Such structures are the preferential pathways for fluid circulation and escape responsible for the precipitation of the authigenic carbonates. Dolomite crusts, nodules and chimneys have been found at several sites in the Guadalquivir and Formosa Diapiric Ridges, on the Cadiz and Guadalquivir channels of the MOW, and on several mud volcanoes and mud cones/diapirs (Iberico, Cornide Faro, Hesperides and Jesus Baraza). Dense fields of dolomite chimneys and aragonite pavements are mainly found at or near the main channel of the outflow of the Mediterranean Water (MOW) west of the Strait of Gibraltar. Aragonite and calcite pavements, typical from cold seeps, have been found associated in the Jesus Baraza, Ginsburg, Mercator, Adamastor, Meknes, Hesperides and Faro mud volcanoes (Figure 1), as well as along the Penn Duick escarpment, in the Moroccan sector. Similar MDAC have also been found in other areas of the Mediterranean Sea, such as the Nile Deep-Sea Fan and the East Mediterranean Ridge (Bayon *et al.*; Gontharet, this volume).

The carbon isotopic composition of the authigenic carbonates ($\delta^{13}C$ = -56.16‰ to -8.42‰ PDB) indicates that they originated from a moderate to extremely ^{13}C depleted reservoir, resulting from the oxidation of methane (Ritger *et al.*, 1987; Paull *et al.*, 1992). The isotopic composition of the MDAC reflects a major mixing of thermogenic and biogenic methane rich fluids with non-methane carbon sources where most probably, seawater is the most important. This is consistent

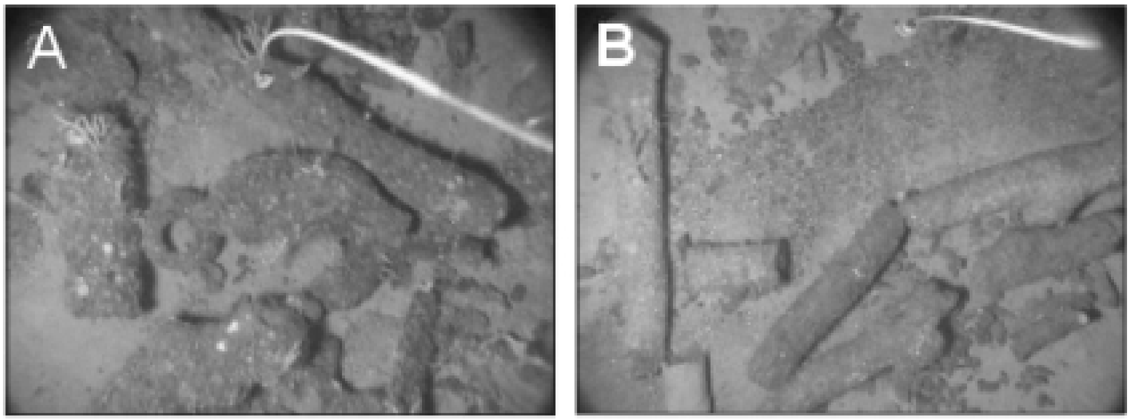

Fig. 3. Underwater video images of the extensive fields of carbonate crusts and chimneys near the Ibérico mud diapir (location in figure 1). The approximate width of each photo corresponds to ca. 1m.

with the gas composition found on several mud volcanoes (Blinova and Stadnitskaia, 2001; Mazurenko *et al.*, 2002; Nuzzo *et al.*, 2004).

The different morphologies of the carbonate chimneys reflect different flow patterns through the sediments in within which they have grown. If a flux of fluid enriched in methane is channellised through the sedimentary column, along borrows, sediment heterogeneities or other conduits, precipitation of the authigenic carbonates will develop at the Sulfate-Methane Transition Zone and the lithification of the sediments along the fluid conduits will result in the formation of dolomitic nodules, crusts and chimneys. Most of these have been found in areas characterized by high backscatter on the side-scan sonar images, particularly along the main channel of the MOW, where the uppermost sediments have been swept by the strong currents. These currents probably removed the sediments within which the chimneys have grown, leaving them lying on the seabed in their present position. The widespread occurrence of MDAC throughout this area is a fossil record of several past episodes of extensive methane seepage in the Gulf of Cadiz.

GAS HYDRATES

Gas hydrates have been recovered from three mud volcanoes in this area: Ginsburg, Bonjardim and Captain Arutyunov (see location in Figure 1). The composition of the gas from the gas hydrates indicates a thermogenic origin which suggests the possible existence of oil fields at depth (Mazurenko *et al.*, 2002).

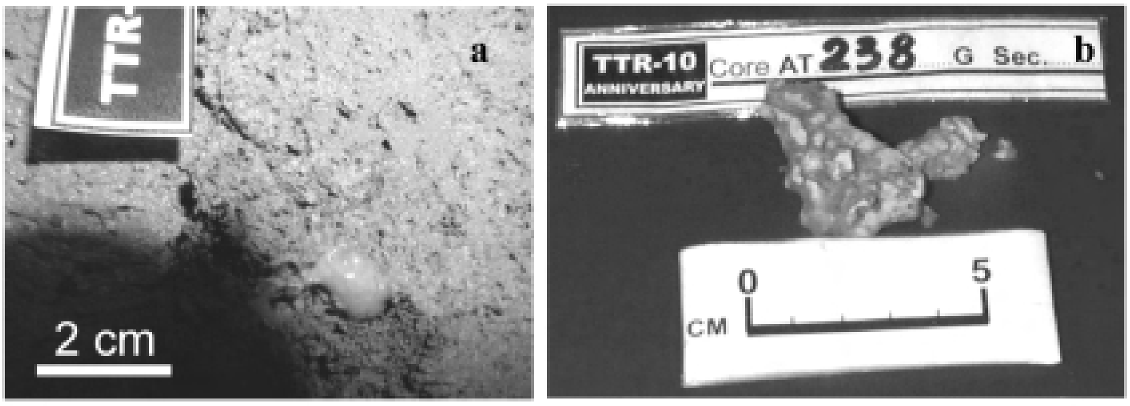

Fig. 4. (**a**) Gas hydrate dissociation in one core from the Captain Arutyunov mud volcano (TTR-12). (**b**) Gas hydrates retrieved from the Ginsburg mud volcano during the TTR-10 cruise, in 1999.

Shallow gas hydrates have also been inferred from geophysical data over the Mercator mud volcano (DePreiter *et al.*, 2005). An anomalous reflection, identified as the base of a gas hydrate stability zone, was observed at the Mercator mud volcano in a water depth of about 400 m. This interpretation was supported by the fact that gas hydrate stability modelling with reported thermogenic gas compositions, indicated that gas hydrates can be stable at this shallow location. BSR-inferred heat flow showed a concentric heat flow pattern around the crater, with a very sharp rise near the crater, consistent with the interpretation that the gas hydrate layer is affected by a focused flow of warm fluid in the crater. Modelled heat flow values near the crater edge run-up to 1100 mW m^{-2} and must be still higher inside the crater (DePreiter *et al.*, 2005).

CONCLUSIONS

The Gulf of Cadiz is characterized by extensive hydrocarbon-rich fluid venting and mud diapirism. It includes numerous mud volcanoes, methane-related authigenic carbonates (crusts, chimneys and carbonate mounds) and pockmarks (Baraza and Ercilla, 1996; Gardner, 2001; Kenyon *et al.*, 2000a, 2001, 2002a; Diaz-del-Rio *et al.*, 2003; Pinheiro *et al.*, 2003; Somoza *et al.*, 2003; Van Rensbergen *et al.*, 2005a). The formation of these structures is related to both the high sedimentation rates during the Pliocene, associated with high subsidence (Maldonado *et al.*, 1999), as well as to the lateral compression due to the Africa-Eurasia convergence, both of which promoted the fluid migration to the surface. The migration of these fluids through the sediments to the seafloor appears, in many areas, to have been controlled by faulting, since most of the mud volcanoes, particularly those in the eastern sector, appear to be located along major NW-SE and NE-SW strike-slip conjugate faults or at the intersections of these faults with the arquate thrusts of the Gibraltar Arc. The migration of the fluids along these faults is possibly related both to along-slope gravitational sliding and to the tectonic compression of the olistostrome and accretionary complex of the Gulf of Cadiz, due to the Africa-Eurasia convergence. Authigenic carbonates are also generally found along several NE-SW oriented mud diapiric ridges in the NE sector of the Gulf of Cadiz, which appear to be controlled by deep strike-slip faults. In the deep Portuguese field, recent results from the TTR-15 cruise, together with new multibeam data collected by the MATESPRO Project show that several mud volcanoes in the deep southwestern part of the Gulf of Cadiz are also aligned and controlled by another set of major WNW-ESE strike-slip faults, associated with the Africa-Eurasia Plate Boundary.

Acknowledgements

The authors thank the NRL, Washington, for kindly having released their SEAMAP mosaic and multibeam bathymetry for this project. Many thanks also to all the participants, the Captain and crews of the various cruises in this area, in particular those from the recent TTR-15 cruise in July/August 2005. The shiptime of the TTR cruises has been jointly funded by the following projects and entities: INGMAR (PLE/4/98, FCT), Euromargins MVSEIS Project (01-LEC-EMA24F; PDCTM72003/DIV/40018), the Belgian TTR-Africa Project and the UNESCO/IOC. PVR participation in this project was funded by FWO-Flanders.

Genesis of cold seeps and mud volcanoes of the Northern Apennine foothills

Rossella Capozzi[1] **and Vincenzo Picotti**[1]

[1] *Dipartimento di Scienze della Terra e Geologico-Ambientali,*
University of Bologna, Bologna, Italy
Centro Interdipartimentale di Ricerca per le Scienze Ambientali, Ravenna, Italy

ABSTRACT

Cold seeps and mud volcanoes in the Northern Apennines foothills, despite their quite regular distribution, can be separated into two main groups on the basis of their geochemical and geological characters: 1) mostly in the Emilia Apennines, topping the upper tectonic nappe of the chain (the Ligurian unit) or 2) in the Romagna Apennines, leaking through the Neogene foredeep units, where the Ligurian unit is absent.

In the Emilia Apennines, mostly thermogenic gas and condensate, associated with formation water, characterize the seepages on top of the upper tectonic nappe of the chain (the Ligurian unit). In the selected case studies the depth of the gas sources has been estimated as over 6000 m, whereas formation water is provided by the shallower foredeep unit of Miocene age. The occurrence of mud volcanoes is mainly associated to deep-rooted normal faults which provide the major escape pathway throughout the Ligurian seal and the Tertiary reservoir.

In the Romagna Apennines, where the Ligurian unit is absent, mainly biogenic gas and saline water are leaking through the Neogene foredeep units. Seepages are associated with shallow permeable carrier beds sealed by Plio-Pleistocene mudstones.

The local geological features play a first-order control on the geochemical characters of the seepages, allowing for very rapid spatial variation of fluids.

Keywords: North-Apennines, mud volcanoes, cold seeps, geochemistry, tectonics.

INTRODUCTION

Cold seeps and mud volcanoes in the Northern Apennines of the Emilia Romagna are aligned approximately along two belts striking NW-SE, close to the main divide and to the foothills respectively (Figure 1). Borgia *et al*. (1986) discussed the origin of many spontaneous fluid emissions mainly on the base of the isotopic composition of gases. In the Emilian sector, gas vents of the main divide belt lie close to the southern limit of the Ligurian unit, the upper tectonic nappe of the Apennine chain, consisting of deformed Tethyan oceanic remnants (Figure 1). The gases have been characterized as thermogenic, with $\delta^{13}C$ values higher than -50 ppt. In the same Emilian sector, on the other hand, the foothill emissions, located at the northern border of the Ligurian unit appear mainly characterized by mixed gas ($\delta^{13}C$ -60, -50 ppt). Biogenic gas is considered as indigenous in the Plio-Pleistocene successions occurring at the foothills and adjacent Po Plain (Mattavelli *et al.*, 1983; Borgia *et al.*, 1986).

We focused our work on selected spontaneous surface seeps along the foothill belt, bearing cold saline waters associated mainly to gas and condensate, locally in the form of mud volcanoes.

We carried out the study of surface geology and seismic profiles (see location of the cross-sections in Figure 1) coupled with the physical, chemical, isotopic and bacteriological analyses of the fluid emissions which were sampled regularly, for some months. Geochemical and isotopic studies aim to provide information about the depth of gas sources and, furthermore, the chemical composition of the saline waters provides additional data for the reconstruction of different migration pathways of fluids. Our goal is unravelling the mechanisms of migration in relation to different reservoir, seal and structural setting.

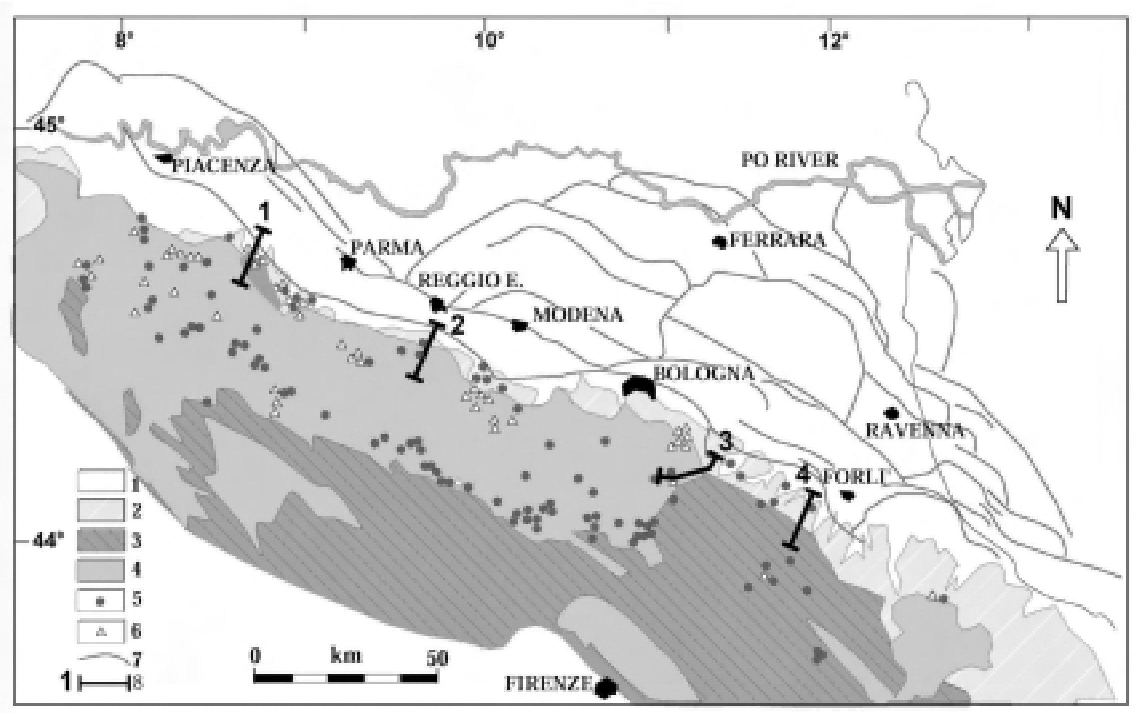

Fig. 1. Geologic scheme and locations of the fluid emissions alongside the Po valley. 1- Continental Quaternary; 2- marine to continental Plio-Pleistocene foredeep units at the foothills; 3- Miocene foredeep units; 4- Ligurian-Epiligurian units; 5- spontaneous fluid emissions; 6- oil and gas from surficial drilled wells; 7- thrust front in the subsurface; 8- trace of the cross-section. Modified after Borgia *et al.* (1986).

MUD VOLCANOES AND COLD SEEPS AT THE NORTHERN APENNINE FOOTHILLS

1. The Emilia sector

The distribution of the studied mud volcanoes and seeps is quite regular along the foothills. Yet these natural emissions can be separated into two main groups from their geochemical and geological characters: i) mostly thermogenic gas characterize the seeps on top of the upper tectonic nappe of the chain (the Ligurian unit) (Capozzi and Picotti, 2002), and ii) mainly biogenic gas is leaking through the foredeep units, where the Ligurian unit is absent.

In the case of the Regnano mud volcano (sect. 2 in Figure 1 and Figure 2) which is a case of the Emilia Apennines, the saline water has low temperature, chlorinity up to 10,000 ppm, pH over 7.8, Eh from -99 to -286, $H_2S > 2$ mg l-1 which can be interpreted as a type of membrane filtered formation water, without meteoric mixing.

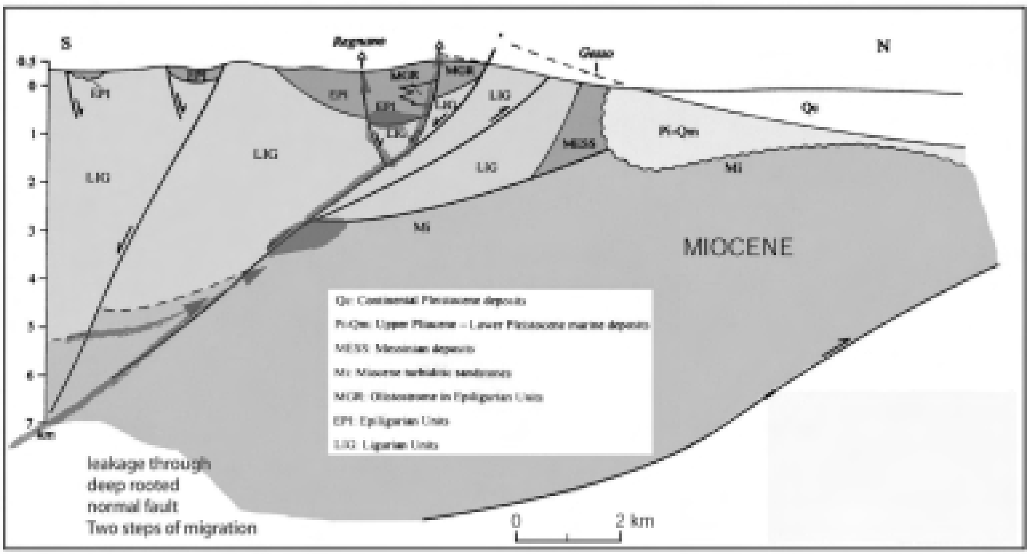

Fig. 2. Cross-section of the Apennine foothills south of Reggio Emilia. The orogenic edifice consists of deformed Miocene clastics overlain by the Ligurian unit and associated Epiligurian deposits, also deformed. The Upper Pliocene - Lower Pleistocene mudstones cap the eroded ramp anticline, finally covered by the continental Pleistocene. A prominent Southwest- dipping normal fault system cuts across the whole edifice, providing a pathway for the fluid migration. Triangles mark the mud volcanoes.

The depth of gas sources must be over 6000 m because of the clear isotopic thermogenic signature ($\delta^{13}C$ (CH4) = - 46.26‰). The Miocene reservoir is sealed by the Ligurian unit (Figure 2).

The Regnano mud volcano as well as the Dragone di Sassuno (sect. 3 in Figure 1; Figure 3) are basically associated to deep-rooted normal faults, which provide major escape pathway

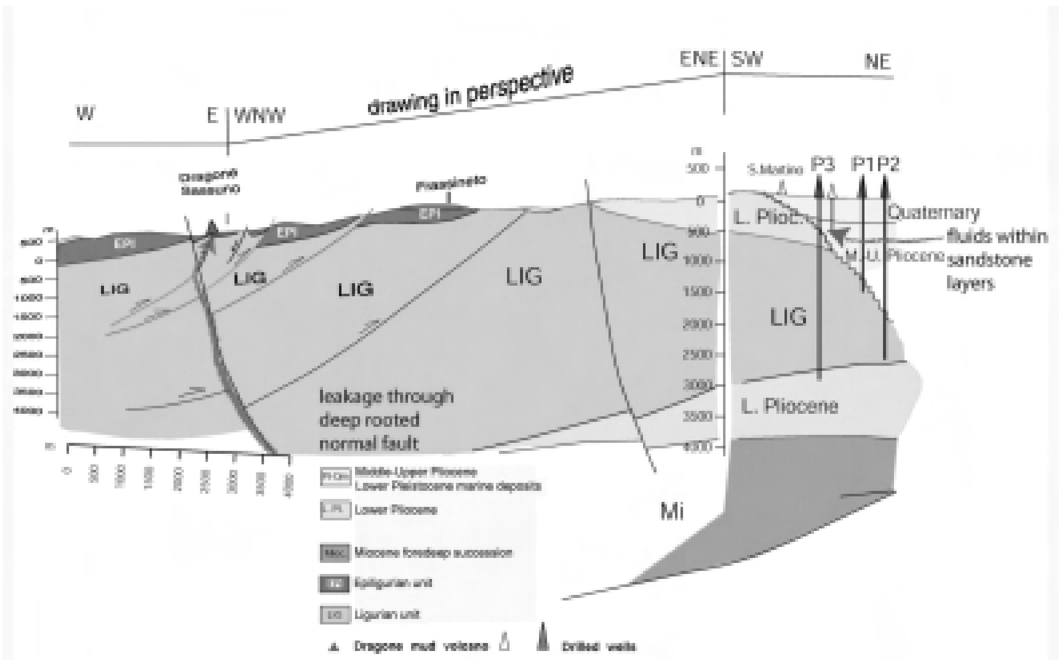

Fig. 3. Cross-section of the Apennine foothills south of Castel San Pietro (Bologna). The Dragone di Sassuno mud volcano shows fluid migration very similar to that of Regnano whereas to the NE, near the Po plain, fluids include recent not filtered formation water, without meteoric mixing, biogenic methane and CO_2.

throughout the seal. Erupted mud is, however, supplied only by the topmost pelitic units (laying maximum 1000 m below the surface) belonging to the Epiligurian succession. The absence of Ligurian deposits in the mud is due to the strong diagenesis associated to a long and complex geologic history of this unit, whereas the Epiligurian units never reached conditions of strong dewatering.

A different geologic scenario, in the frame of the above described system, is that of Salsomaggiore, between Parma and Piacenza (sect. 1 in Figure 1; Figure 5). In this province, spontaneous fluid emissions and drilled wells are very rich in high saline water, methane and condensates. The chemical composition of the water is in the range of "membrane concentrate saline water" (*sensu* White, 1965) (Figure 4).

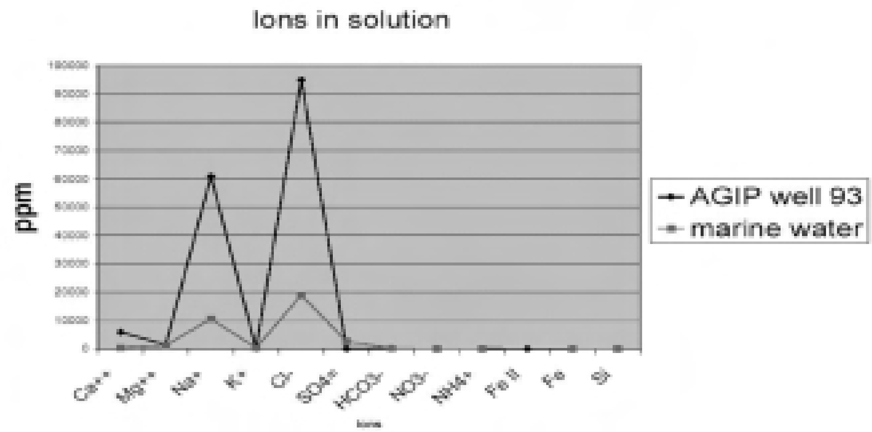

Fig. 4. Major ions in solution in the water of the Agip well 93 at Salsomaggiore.

At Salsomaggiore, a ramp brachi-anticline, consisting of Miocene clastic units, is characterized by a plunge toward SE. The Salsomaggiore structure, in fact, has been produced by compressions with vergences to the NE, corresponding to the main strike of the Northern Apennines (Figure 5), but also to the NW.

Stratigraphic reconstruction indicates a Serravallian age for the growth of this anticline which was sealed by a thin sheet of Ligurian, now completely removed by erosion. Thanks to the presence of a marly unit, however, the top of the anticline represents an efficient trap for deep fluids migrating via up-dip carrier beds, principally from S and SE.

2. The Romagna sector

In the Apennine foothills of Romagna, never covered by the Ligurian unit, except for the Marecchia valley, biogenic methane emissions occur within deformed Upper Neogene foredeep units, which represent an uplifted portion of the main hydrocarbon system exploited in the Eastern Po Plain. The Pliocene and Pleistocene succession of foothills dips to the Po Plain (NE) and acts as an effective carrier for gas and formation water generated in the adjacent sector (cross-section 4 in Figure 1; Figure 6) with some meteoric mixing.

The location of these natural seepages appears controlled mainly by the presence of good- quality reservoirs, such as the Pliocene calcarenites (the so-called Spungone) cropping out south of Forlì (Capozzi and Picotti, 2003). In this reservoir, the biogenic methane is likely supplied by a sapropel-bearing interval of about 60 m in thickness. Generally, in the Romagna sector of the Northern Apennines the emissions are concentrated within the valleys, which are first reached by the buoyancy migration.

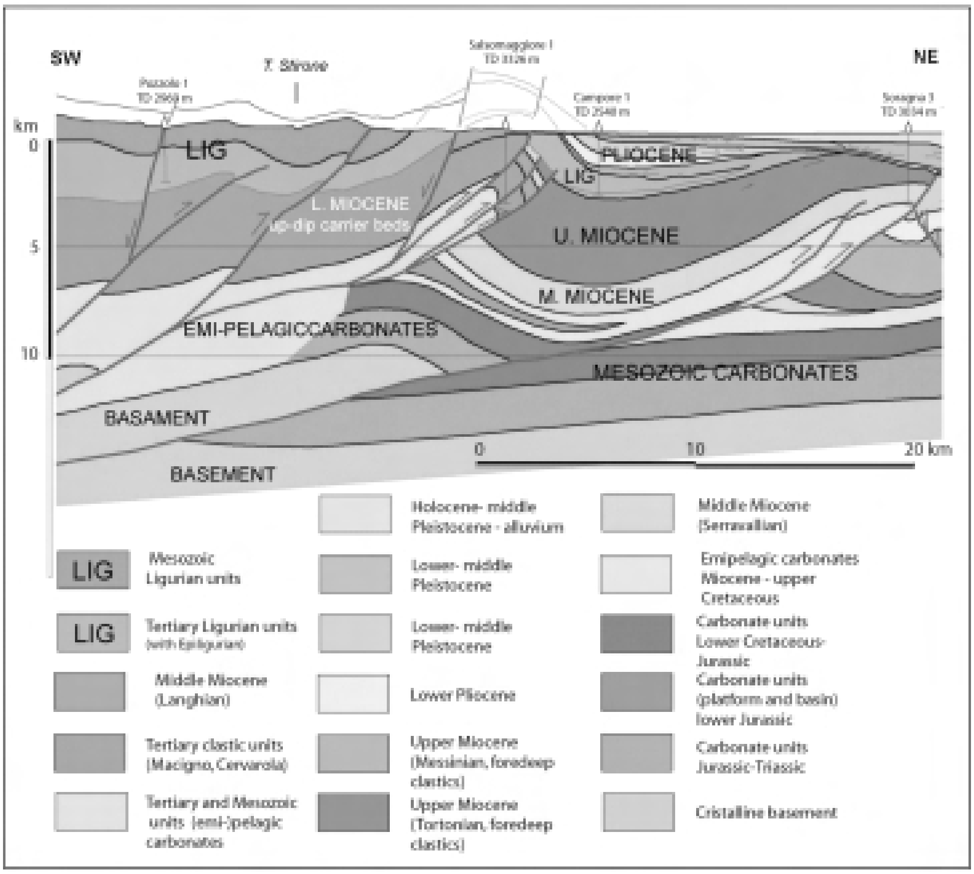

Fig. 5. Cross-section of the Apennine foothills of Salsomaggiore. The orogenic edifice consists of deformed Miocene clastics overlain by the Ligurian unit and by upper Neogene toward the Po Plain. On the eroded Salsomaggiore anticline a Langhian marly unit provides the present seal. Fluids likely migrate from S-SE where they are undergoing to the higher burial.

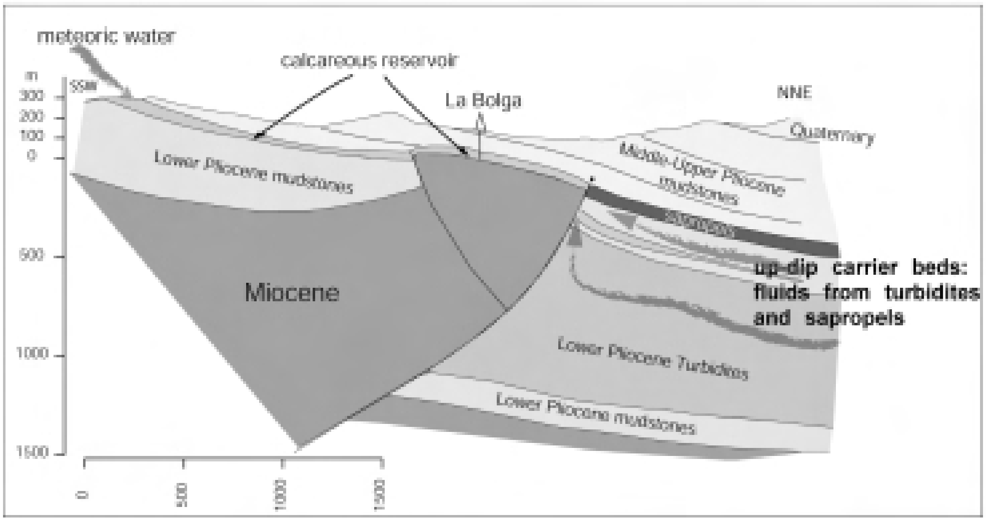

Fig. 6. Cross-section of the Apennine foothills south of Forlì. The edifice consists of deformed Miocene foredeep clastics overlain by Plio-Pleistocene mudstones with intervening calcarenites. This latter provide the reservoir for formation water and methane migrating up-dip from North toward the foothills.

CONCLUSIONS

Information collected along the foothill belt of the Northern Apennines indicates a wider spectrum of seepage types than previously described. Methane and water composition in the Emilia sector testifies the presence of deep sources and permeable horizons down to 6-7 km under the surface. Fluids escape is driven by the presence of deep rooted normal faults generated by an extensional state of stress, which coexists with a deeper compressive one, or by buoyancy following up-dip carrier beds.

In the case of absent Ligurian, as in the Romagna sector, seepages are associated with shallow permeable carrier beds sealed by Plio-Pleistocene mudstones. The hydrocarbon sources and reservoirs happen together in these younger and shallower clastic successions. Furthermore, the role of the tectonic structures in this area appears less important.

Multi-scale seafloor mapping of active seep-related structures, offshore Egypt

Stéphanie Dupré[1], John Woodside[1], Ingo Klaucke[2], Jean Mascle[3], Jean Paul Foucher[4] and the NAUTINIL & MIMES Scientific Parties

[1] *Faculty of Earth and Life Sciences, Vrije Universiteit, Amsterdam, The Netherlands*
[2] *IFM-GEOMAR, Research Center for Marine Science, Kiel, Germany*
[3] *Geosciences Azur, Villefranche-sur-mer, France*
[4] *Ifremer, Plouzané, France*

ABSTRACT

The Nile Deep Sea Fan system presents a rich variety of fluid escape structures, gas chimneys, pockmarks and carbonate crust mounds, brines pools, and several types of mud volcano. These seep-related structures were explored for the first time with the Nautile submersible during the 2003 Nautinil expedition and are characterized by high thermal gradients and highly gas-saturated sediments. More recently, high resolution side scan sonar data acquired during the 2004 Mimes expedition brought more detail to the geophysical imagery. The EdgeTech DTS-1 deep tow sonar coupled with a 2-8 kHz chirp subbottom penetrator was deployed around 100 m above the seafloor and operated at a frequency of 75 kHz. Several gas plumes were acoustically detected in the water column of the side scan record both in the Eastern and Central Provinces, e.g. above Isis and Amon mud volcanoes and numerous pockmarks. These observations confirm the intensity of the present-day activity offshore Egypt in terms of seepage associated with gas emissions and its continuity through time. The geophysical signature of these active sites, commonly associated with high backscatter, presents however some variability in the signal depending on the intensity and the type of seep-related structures, e.g. the presence of relatively young mud breccia or authigenic carbonate crust pavements. Acoustic mosaics of the seafloor and chirp profiles reveal subsurface sediments commonly disturbed by ascending fluids throughout the delta and usually marked by seafloor carbonate crust structures. In the Eastern Province, the wide gas chimneys, formed during successive episodes of mud extrusion associated with relatively low volume of mud breccia, are systematically associated with carbonate crust formation. The feeder channels of these mud volcanoes, similar to the gas conduits below carbonate crust structures identified over the entire delta, are relatively narrow and, for the vast majority of them, do not exceed a few tens of metres in diameter. These seep-related structures, gas chimneys and carbonate crust structures are controlled by the local and regional tectonics in connection with a complex fault network, deeply rooted faults, and shallower ones associated with salt tectonics for instance.

Keywords: Nile Deep Sea Fan, gas chimneys, mud volcanism, authigenic carbonate crust, backscatter, free gas emission.

BACKGROUND

The eastern Mediterranean Sea is, like many other marine areas, subject to significant seepage activity. Mud volcanism, authigenic carbonate crust formation, chemosynthetic communities of macro-organisms and microbes, e.g. anaerobic bacteria and archea, characterize these areas. The first occurrence of seepage associated with mud volcanoes and brines was discovered in the early eighties along the Mediterranean Ridge, the accretionary prism of the Hellenic Arc (Cita *et al.*, 1981). Since then, more and more seep-related structures have been identified on the seafloor, e.g. in the Anaximander Mountains (Woodside *et al.*, 1998; Lykousis *et al.*, this issue), along the Florence Rise (Woodside *et al.*, 2002; Zitter, 2004), in the Levant Basin (Coleman and Ballard, 2001), and in the Nile Deep Sea Fan (Bellaiche *et al.*, 2001; Mascle *et al.*, 2001). Bathymetric and acoustic imagery maps of the seafloor obtained with multibeam echosounder are essential databases for identifying fluid venting areas as a basis for further investigations (Loubrieu *et al.*, 2001; MediMap Group *et al.*, 2005).

Seep-related structures were identified and mapped offshore Egypt using multibeam data and limited seismic and coring data (Figure 1) (Loncke *et al.*, 2004; Sardou and Mascle, 2003). The Nile Deep Sea Fan can be divided into three distinct morpho-structural Provinces. The western Province, the most currently active part of the delta, is characterized by numerous small scale mud volcanoes and a few wide calderas and gas chimneys. Seafloor in the Central Province is subject to slope instabilities and sedimentary slides, and is scattered with numerous pockmarks, and carbonate pavements and mounds. The Eastern Province, delimited on the western side by a major transgressive fault zone, is strongly controlled by salt tectonic activity. Gas chimneys are not restricted to one of these provinces, but are located in the upper slope domain along the present day continental platform boundary or close to the limit of the Messinian platform.

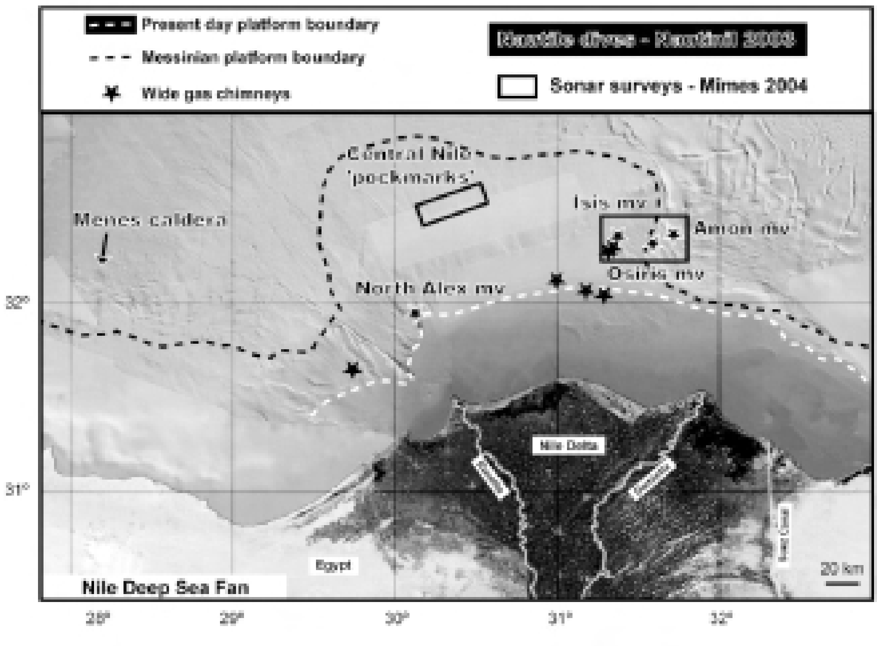

Fig. 1. Nile Deep Sea Fan shaded morphology modified after Loncke and Mascle (2004) and Sardou and Mascle (2003).

The rifting episodes and the Messinian salinity crisis are crucial events in the tectonic history of the Nile Delta, especially concerning the formation at depth of hydrocarbons and the occurrence at the seabed of seepage activity. Along the rifted continental Egyptian margin, sedimentary basins experienced rapid subsidence and high sedimentation rates, leading to the burial of uncompacted sediments, and eventually, to the formation of hydrocarbons. The deposition of thick evaporites above such reservoirs was essential to maturation by sealing the petroleum system. The accumulation of gas and oil combined with water and mud were later released through fault conduits, generating fluid expulsion or diffusion through the seabed. Faults associated with salt tectonics represent preferential pathways for fluids to escape. Additionally, during the Messinian, the margin was incised by large scale canyons, and infilled later on by Pliocene sediments forming important reservoir rocks (Abdel *et al*., 2001; Dolson *et al*., 2002). At present, the Nile Deep Sea Fan forms a sedimentary edifice more than 10 km thick (Abdel *et al*., 2001; Mascle *et al*., 2003).

NEW DATASETS AND DISCOVERIES

The Mediflux Project, promoted by the European Science Foundation, is a scientific programme dedicated to an integrated study of seepage through the seabed of the Nile Deep Sea Fan. Gathering scientific teams from the Netherlands, France and Germany, this programme is strongly based on marine expeditions and acquisition of new biological, geological and geophysical datasets. During the first NAUTINIL campaign onboard the R/V *L'Atalante* in 2003, the French Nautile submersible was operated (Figure 2) and, for the first time, fluid seep-related structures were observed *in situ* offshore Egypt, along with sampling and measurements. The second cruise MIMES, onboard the Dutch vessel *Pelagia* in 2004, investigated several targets in the Central and Eastern Provinces between water depths of 700 to 1800 metres with the German DTS-1 (EdgeTech) deep tow side scan sonar (75 kHz) coupled with a 2-8 kHz chirp subbottom penetrator (Figure 2). The third and last cruise of the Mediflux programme, BIONIL, will be held in the autumn of 2006 onboard the R/V *Meteor* with the operation of the German ROV Quest and the French AUV Aster^{X}.

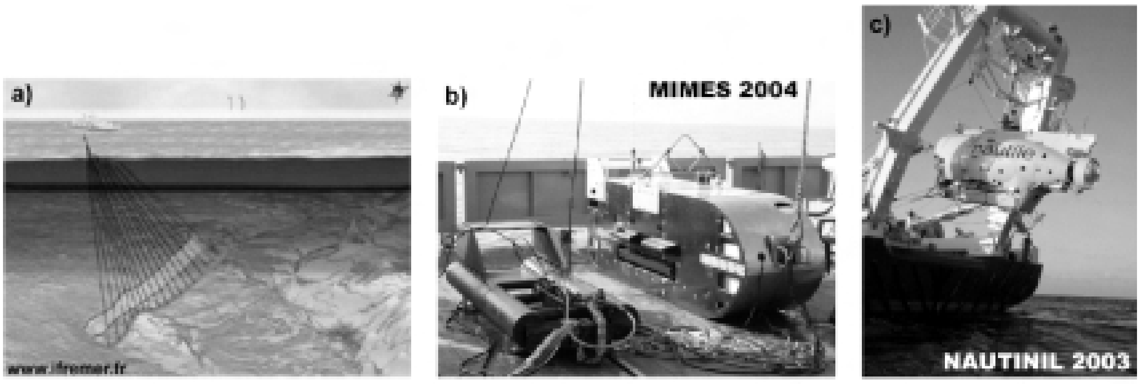

Fig. 2. Multi-scale seafloor mapping and acquisition tools **a**) Bathymetry and seafloor reflectivity obtained with multibeam echounder, e.g. Simrad EM12 (13 kHz). **b**) Backscatter imagery of the seafloor using deep tow side scan sonar, e.g. DTS-1 EdgeTech (75 kHz). **c**) *In situ* observations and measurements at the seafloor with submersible, e.g. the French Nautile (Ifremer).

Evidence of seepage activity over the entire delta was confirmed, and observed in great detail in the three explored target areas: the Menes caldera in the west (including Chefren and Cheops mud volcanoes, see Huguen *et al*., this issue), the central pockmarks (Bayon *et al*., this issue), and the four wide gas chimneys roughly located along a belt close to the continental platform boundary (North Alex, Isis, Osiris and Amon mud volcanoes) (Figures 1 and 3). The seabed is heavily disturbed by fluid venting-related structures which cover a significant surface of the offshore delta. The spectacular intensity of these fluid emission systems was recorded by ground truth geological, sedimentological, (micro)biological, geochemical and geophysical data, revealing high gas concentration in the sediments, sulphate reduction and anaerobic methane oxidation at the subsurface (see Gontharet, this issue), high thermal gradients in the surface sediments (e.g. 40°C at 10 m depth below seafloor at the active centre of the Isis mud volcano (Foucher *et al*., 2005; Feseker *et al*., this issue) and in the brines (e.g. 57°C at Chefren through 250 m of briny mud, Woodside *et al*., 2005), numerous high backscatter patches on the seafloor (Figure 4b) commonly associated with seismic gas wipe outs, acoustic plumes of free gas bubbles (Figure 4a), and methane and higher hydrocarbons enriched water column (de Lange *et al*., this issue). The diversity of the seep-related structures at the scale of the submarine delta is remarkable. Brine pools on mud volcanoes in the caldera structure, small-scale mud volcanoes, pockmarks and carbonate crust pavements and mounds, and wide gassy mud chimneys, characterise parts of the seafloor of the Nile Deep Sea Fan, often together (Figure 3).

Fig. 3. Nile Deep Sea Fan seafloor pictures taken from the Nautile submersible in three active seepage sites. **a**) Warm brine pool flows, with (sulphur/ bacterial?) white filaments on top of Chefren mud volcano, located inside the western Menes caldera. **b**) Fracturated carbonate crust turtle-back structures in the Central Nile, partly covered with a thin layer of hemipelagic sediments. **c**) Fresh mud breccia at the active centre of the Amon gas chimney.

Geological mapping of seafloor morphology, seepage and related (micro)biological activity for instance, primarily based on ground truth observations along the submersible tracks, additionally provides crucial constraints for calibration of geophysical seafloor signatures, i.e. reflectivity from the multibeam echosounder and backscatter from the deep tow side scan sonar. A possible value of such a calibration is to extend geological mapping into unexplored areas and thus to be able to estimate the seepage activity and to predict the nature of the seafloor and shallow subsurface, for example, as well as the occurrences of mud volcanism or carbonate crust formation. Moreover, seafloor mosaics created from surveys using several geophysical tools

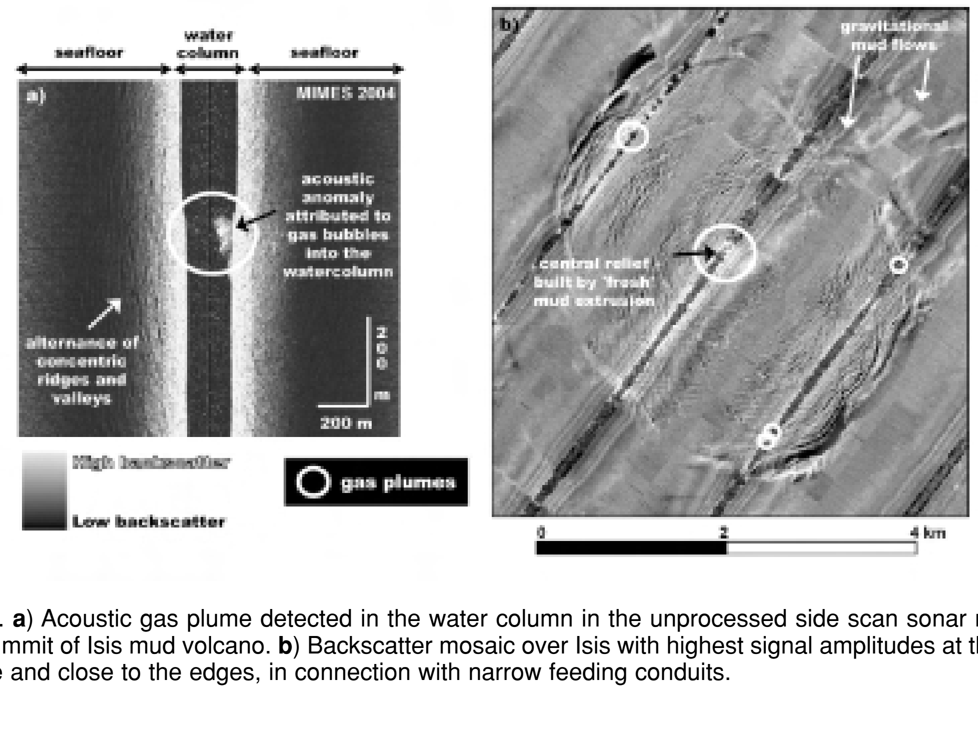

Fig. 4. **a**) Acoustic gas plume detected in the water column in the unprocessed side scan sonar record at the summit of Isis mud volcano. **b**) Backscatter mosaic over Isis with highest signal amplitudes at the active centre and close to the edges, in connection with narrow feeding conduits.

operating at different frequencies (e.g. 13 and 30 kHz respectively for the Simrad EM12 and EM300 multibeam echosounder, 75 or 410 kHz for the DTS-1 EdgeTech side scan sonar) do not image geological targets in the same way due to higher penetration of low frequency emitted signals (at least 1.8 metres and less than 70 cm respectively for the EM12 and EM300, and not more than a few tens of centimetres for the DTS-1) and different resolutions. Comparative study of these multi-spectral datasets may for instance aid identification of different successive stages in mud volcano formation.

GAS CHIMNEYS AND MUD VOLCANISM

Mud volcanoes investigated on the Nile Deep Sea Fan are located at the edge of either the present-day (North Alex) or Messinian continental platform boundary (Isis, Osiris and Amon) between 500 and 1100 metres water depths (Figure 1). They correspond to large sub-circular structures of a few km in diameter with very low relief, from 50 to 100 m on average, of flat or slightly conical shape, and very gentle slope (between 1° and 4°).

The mud breccia is highly gas saturated, containing essentially numerous small millimetric clasts. Gas analysis from sediment and water samples reveal a thermogenic origin of the methane and other hydrocarbons for the vast majority of the different explored sites (Mastalerz *et al*., 2004; Prinzhofer *et al*., 2005). Degassing, spontaneous or triggered, observed directly at the seafloor from the submersible, characterizes the central seepage zones, and additionally, several peripheral active sites. The sediments at these seeps are dark grey to black due to sulphate reduction and are commonly partly covered with white mats of inorganic precipitates and/or bacterial origin (e.g. *Beggiatoa* mats). The fluid venting structures observed *in situ* are systematically associated with a high backscatter signature on the sonar mosaic (Figure 4b) due to the high gas concentration, the recently extruded mud breccia edifice, and carbonate crust structures. Furthermore, several gas plumes were inferred in the water column in the side scan sonar record, either at the centre of the volcano where activity was known and/or on the edges (Figure 4a). These acoustic anomalies correspond to the presence of gas bubbles in the water column, enriched mainly in methane. CTD casts recovered above the centre of Isis for instance indicate a concentration of CH_4 of 600 ppmv at 50 m above seafloor (Mastalerz *et al*., 2004). The subsurface sedimentary layers of these active volcanoes, imaged by chirp profiles, represent a uniform and chaotic seismic facies without any internal structure, attributed to the mud breccia; and they are associated with gas wipe outs and sometimes with narrow vertical gas conduits reaching the seafloor. Although gas saturated sediments at the seafloor are restricted to a few locations in connection with these narrow conduits, and neither coring nor heat flux revealed much activity in the periphery of the active sites, the entire structure of these volcanoes is much saturated in gas at depth.

The subsurface morphology of the different mud volcanoes exposes an alternance of relatively concentric ridges and gullies, caused by relatively slow mud extrusion which shapes the surface of the volcano and causes these irregularities (Figure 4). Catastrophic mud eruption events are unlikely even if mud extrusion probably experiences episodic and significant events. Mud flows identified on the multibeam reflectivity maps in the close proximity of the mud volcanoes represent mass flows and not erupted mud flows, and correspond rather to gravitational collapse (Figure 4b).

Active seepage is not restricted to a single primary location on a mud volcano. In other words, the main activity is not necessarily confined to the centre alone, but seep-related structures have been observed and/or identified on sonar mosaic and subbottom profiles on the flanks of the volcano or at the edges (Figure 4b). Additionally, the main centre of the mud volcano activity is not necessarily the geometric centre of the structure (e.g. Osiris). The occurrence of seepage here and there at the seabed is tectonically controlled (see Huguen *et al*., this issue), as is their localization on the delta and the overall shape and morphology of fluid venting structures; and therefore they may vary from one mud volcano to another.

Mud volcanism appears to be closely associated with the formation of authigenic carbonate crust. Mud breccia in the centre of North Alex for instance exhibits small scale carbonate concretions (mm to 2 cm clasts). The western flank of Amon is partly covered with carbonate structures, chimneys, turtle-backs, pavements or massive metre-scale blocks, easily identified in reflectivity, backscatter, and chirp data. The other mud volcanoes are characterized by isolated and restricted carbonate crust structures located around the edges of the volcano and/or at the peripheries. Similarly to the narrow feeder channels connected to mud and fluid ascension, the seeps where carbonate crust forms, are underlain at depth with numerous narrow vertical gas conduits.

SEEPAGE AND AUTHIGENIC CARBONATE CRUST FORMATION

Observed *in situ* in the Central (Figure 3b) and Eastern Provinces, structures associated with the formation of authigenic carbonate crust correspond to active seep environments in which are found benthic communities of (macro)organisms (e.g. vestimentiferam tubeworms, lucinidae shells). Such fluid venting structures, characterized by highly gas saturated sediments, were identified additionally and extensively on acoustic seafloor mosaic and chirp subbottom profiles. Carbonate crust structures correspond to very high backscatter from subcircular features of a few metres to a few hundreds of metres in diameter. We observe a relatively high variability in the backscatter amplitude which is related to the presence of different types of carbonate crust structures and activity, e.g. small scale pockmarks of 10-20 m diameter or thin carbonate layers partly covered with hemipelagic sediments. Several gas plumes were detected acoustically in the water column in the side scan record above pockmarks and carbonate crust mounds in the Central Delta at water depths of ~1700 m, and above the western flank of Amon mud volcano.

The formation of these structures is not restricted to the surface of the mud volcanoes, the edges, or the close vicinity. They are associated with several fault networks in the Eastern Province, along the major transpressive fault running N010 and faults related to salt tectonic activity (N020-030 and N320-330), and on the Messinian platform along ~N340 orientated faults in connection with large scale Messinian canyons, or possibly associated with slope instabilities in the Central Province.

Carbonate crust edifices occur most commonly in gentle depressions and associated with narrow gas conduits, similarly to the main fluid pathways imaged below the wide Eastern mud volcanoes. On the chirp profiles of the Central Nile, inferred gas conduits vertically cut the sedimentary reflections down to 50 m at least. They correspond mostly to narrow and localized cylindrical columns of a few meters to 10-20 m diameter, sometimes up to 100-200 m wide and with exception reaching 400 m. Seafloor depressions are commonly observed above highly disturbed sediments caused by upward gas migration.

CONCLUSIONS

The Nile Deep Sea Fan is an area of very active seepage with a great diversity of fluid venting structures associated with mud volcanoes, gas chimneys, brines and carbonate crust formation. These ubiquitous fluid escape structures are the sites of methane release into the water column and possibly, especially in shallower upper slope domains, into the atmosphere. Subsurface sediments are commonly disturbed by ascending fluids throughout the delta, and these are usually marked by seafloor carbonate crust structures.

The wide mud volcanoes, so-called gas chimneys, are systematically associated with carbonate crust formation, predominantly on the mud volcano summit, on the edges or close to this edifice. The feeder channels of these mud volcanoes, similarly to the gas conduits below carbonate crust structures identified over the entire delta, are relatively narrow and, for the vast majority of them, do not exceed a few tens of metres in diameter. The large mud volcanoes offshore Egypt form most likely during successive episodes of mud extrusion associated with relatively low volume of mud breccia. Catastrophic eruption events with ‘running’ mud flows are unlikely. Mud flows around the mud volcanoes correspond rather to gravitational collapse.

Seep-related structures, gas chimneys and carbonate crust structures, are not randomly localized on the Nile Delta, they are controlled by the local and regional tectonics, as is the overall shape of the mud volcanoes. Several fault networks shape the seepage distribution offshore Egypt. In the Eastern Province, concentrations of seeps are clearly connected to the major transpressive fault running N010 and (growth) faults in relation with salt tectonic activity oriented N020-030 and N320-330. On the Messinian platform, seeps are aligned along ~N340 orientation in connection with large scale canyons or associated with slope instabilities in the Central Province.

Acknowledgements

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Mud/Brine expulsions on the Nile Deep Sea Fan: Geophysical characterization and in situ dive observations of mud mounds in the Menes Caldera

C. Huguen[1,2], J.P. Foucher[3], J. Mascle[2], L. Loncke[4], H. Ondreas[3], M. Thouement[3] and the NAUTINIL Scientific Party

[1] *LEGEM, Université de Perpignan, Perpignan, France*
[2] *Géosciences Azur, Observatoire Océanologique, Villefranche-sur-mer, France*
[3] *DRO/GM Ifremer, Plouzané, France*
[4] *UPJV Faculté des Sciences, Laboratoire Sciences de la Terre, Amiens, France*

ABSTRACT

Based on geophysical and *in situ* observations made during the FANIL (September 2000) and NAUTINIL (September-October 2003) cruises, we present a detailed analysis of fluid-escape geological structures of the Nile Deep Sea Fan (NDSF). We focus on the western province where multibeam data show a broad area with numerous mud cones, 300-900 meters wide and several tens of meters high.

The studied area is the Menes Caldera, a sub-circular foundered portion of the sea floor, about 8 km in diameter, bounded by steep 50-60 m high walls, and lying at about 3020 m water depth, where three of the most prominent cones have been identified: CHEOPS, CHEFREN and MYKERYNOS. Unlike mud volcanoes commonly detected over active margins (Huguen *et al*., 2004), these features are not characterized, on backscatter records, by highly reflective patches (Loncke *et al*., 2004); they however show stronger acoustic backscatter signature than the surrounding seafloor; this was considered as indicative of probable active fluid venting, recent mud flows and/or diagenetic carbonate crusts.

During the NAUTINIL expedition, the first two exploratory dives allowed to identify the most active areas in terms of fluid-brine seepage; these are located at the top of the observed mud cones; complementary dives were then dedicated to detailed studies, including *in situ* sampling and various physical and chemical measurements.

This presentation illustrates occurrences of: **(1)** active brine seeps, **(2)** diagenetic carbonate crusts, **(3)**, recent or ancient mud flows and, **(4)** associated fauna and bacterial mats.

Major results relate to the presence, on two of the mud mounds, of massive active brine/mud expulsions over areas reaching 3,200-300m in diameter. On the two mud mounds, a concentric

zonation of the fluid activity has been observed, including a central domain characterized by dark brine/mud mixture emission vents, and peripheral overflows of almost transparent brines. The brine overflows form sub-circular brine lakes around the mud mounds summits. Large surfaces of the brines exposed at the seafloor are covered by whitish bacterial mats. Filamentous bacterial mats are carried down the slopes of the mounds by the brine/mud overflows. Outside the central active areas, the outer slopes are characterized by a gently sloping, uniformly ochre, seafloor. Thin carbonate pavements associated with tube worms and gastropods locally occur close to the active area.

Key Words: Nile Deep Sea Fan, mud cones, fluid seepage.

INTRODUCTION

The Nile Deep Sea Fan was built mainly in the past several million years since the Messinian salinity crisis and covers a large segment of the ancient (late Jurassic to early Cretaceous) passive margin of Egypt. This huge sedimentary pile appears intensively deformed, due to both the complex geodynamic setting of the Eastern Mediterranean, and important salt-related tectonic processes triggered by the presence of thick ductile evaporite layers over most of the NDSF actual extend. In close connection with both tectonic processes, a large number of fluid seeps and mud constructions have been discovered during the last five years over the Egyptian margin continental slope (Barsoum *et al.*, 2000; Mascle *et al.*, 2000; Coleman et Ballard, 2001; Dimitrov and Woodside, 2003; Loncke *et al.*, 2004).

This paper focuses on three of the mud cones identified within a wide (about 50Km by 100 km) field of structures over the NDSF western province (Figure 1). From the bathymetric data collected over this area (Loncke *et al.*, 2004), these structures are characterized by conical shapes, with diameters between 200 and 1,000 m, for maximum elevations not exceeding a few tens of meters. Parts of them show a collapsed summit, which forms a small scale crater at the top of the structure. These features appear either isolated and scattered on the NDSF seafloor or located within large scale negative reliefs, so called "calderas" (Figure 1). Unlike the commonly described mud volcanoes over active margins (Woodside and Volgin, 1996; Huguen *et al.*, 2004), these features do not show large highly backscattering mud flows. The summit area of these structures appears however characterized by a stronger acoustic backscatter than the surrounding seafloor, which could reveal probable active fluid venting, recent mud flows or diagenetic carbonate crusts.

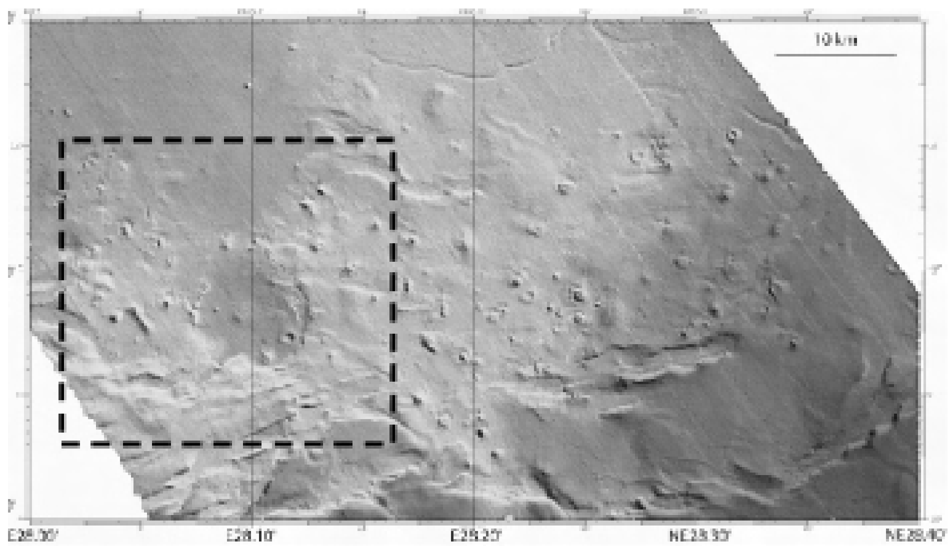


Fig. 1. Bathymetry of the Western Nile Deep Sea Fan province (FANIL data, Loncke *et al.*, 2004).

THE MENES CALDERA

The Menes Caldera, is one of the most clearly observed structures on the bathymetry map of the Nile Deep Sea Fan (see location on Figure 1). It is a large seafloor crater of about 8 km in diameter with steep surrounding walls, except to the north, and a basin depth of about 3,020 m (Figure 2a). Seismic profiles indicate that the structure has some fault control (Loncke *et al.*, 2004), possibly related to underlying salt movement, and what appear to be gas chimneys at least below a central cone as well as below a cone on the southern fault-controlled edge of the structure. There are a four or five well-defined cones around the edge of the structure and one in the centre, all with low local relief of from 10 to 40 m and widths of 500 – 1,000 m. All cones show elevated backscatter at the summit, suggesting recent mud/fluid seepage activity (Figure 2b). For the detailed investigations during the NAUTINIL cruise, the three more prominent structures, named CHEOPS, CHEFREN and MYKERYNOS, have been chosen as main targets. Complementary areas of interest were the rim of the caldera, as well as its basin floor where it was thought, because of a weak acoustic backscatter in the EM12D imagery (Figure 2b), and the presence of salt below, that there might be brine lakes. Two exploration dives allowed identifying the main active areas of the Caldera, which seems to be the summit area of the mud cones, where complementary dives dedicated to a more detailed analysis and to *in situ* sampling and measurements have been focused.

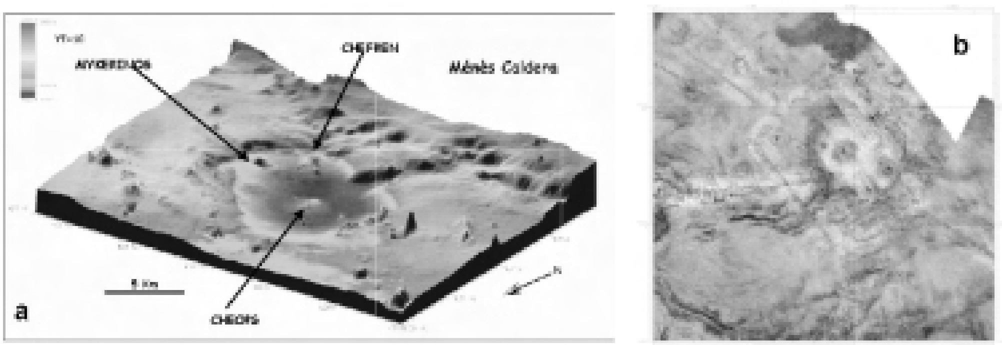


Fig. 2. 3D view (**a**) and backscatter data of the MENES Caldera (**b**) from NAUTINIL data (2003), see approximate location on Figure 1.

CHEOPS MUD MOUND

The outer slope of the CHEOPS mud cone is characterized by a gently sloping uniformly ochre seafloor, crossing a few small hills and getting gradually shallower towards the centre of the volcano. Interestingly, when getting closer to the centre, thin carbonate pavements are observed as well as small tube worms (a few cm long) and gastropods seen in abundance on the ochre seafloor up to the sharp and steep edge of an important brine lake curving around a central dome covered by black sediments (Figures 3a,3c). Currents observed in the brine also indicate that there is a likely outflow region somewhere, perhaps where the outer margin has approached steeper slopes further from the centre. White filamentous material could be seen everywhere suspended in the lake, or lying on the bottom, and showing signs of movement. In places, black patches on the bottom of the brine lake are thought to be small springs bringing fluids and mud into the lake. The central part of the volcano that emerges out of the brine is clearly an area of young mud/brine eruption. Several eruption centers (Figure 3b), several tens of cm to several meters in diameter were identified and all attempts to sample it with a push core or a box corer failed, due to a surprisingly fluid mud. This central dome has a very gentle slope into the brine lake, generally covered by white fluffy material thought to be bacterial mats. Evidence both for fluids running down the side of the dome and for the sources of these fluids were observed, as well as a number of small rivulets suggesting fluid movement down the side of the dome.

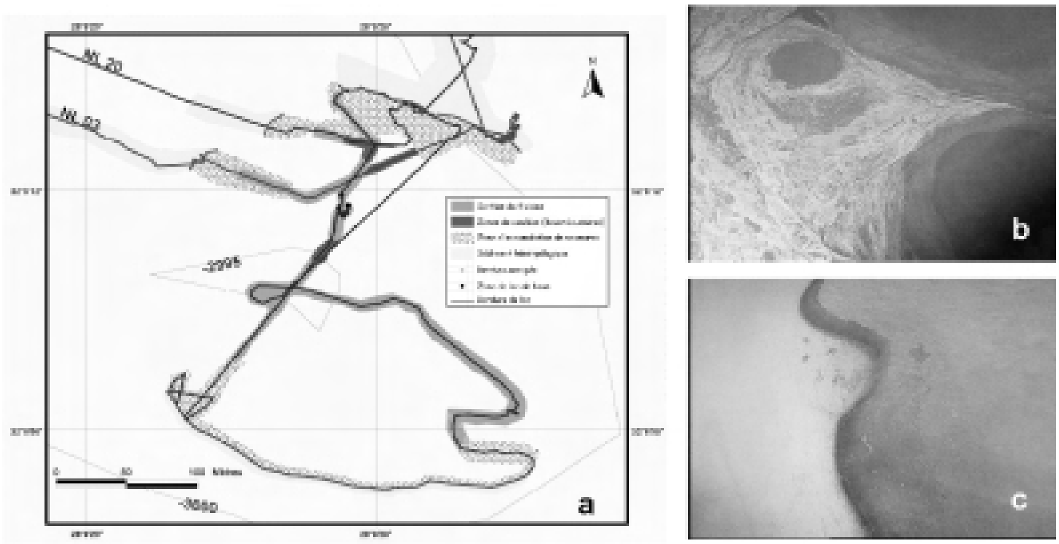


Fig. 3. (**a**) Interpretative geologic map of the CHEOPS summit area (deduced from NAUTINIL dives interpretation); (**b**) central mud/brine expulsion domain; (**c**) boundary between the brine lake and the surrounding pelagic seafloor.

CHEFREN MUD MOUND

As observed for the CHEOPS mud cone, interpretation of the dives conducted on CHEFREN indicates outer flanks covered by light brown pelagic sediments and a central active area of about 200 m in diameter (Figure 4a). Within the central area, a large domain of fluid expulsions is identified, with overflows of a mud/brine mixture out of the central zone (Figure 4b). This mixture is slightly replaced by transparent brine flows and rivers being accumulated within an arcuate brine lake at the southern boundary of the central area (Figure 4a). Important covering of this central mud/brine expulsion zone by bacterial mats is also observed, disturbed by several circular mud expulsion centres. Unlike on the CHEOPS structure, important mushrooms like bacterial formations are observed at the periphery of the central active zone, directly covering the pelagic sediments (Figure 4c) and connected with local orange mineral deposits.

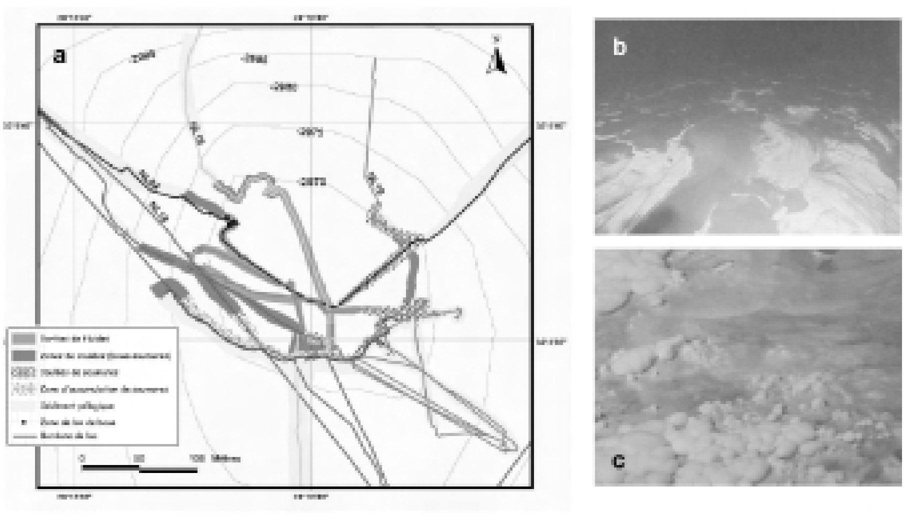


Fig. 4. (**a**) Interpretative geologic map of the CHEFREN summit area (deduced from NAUTINIL dives interpretation); (**b**) central mud/brine expulsion domain; (**c**) mushroom like bacterial mats covering the seafloor at the periphery of the central active area.

MYKERINOS Mud mound

Unlike the two previously described mud cones, no particular fluid venting evidence (mud/brine flows, bacterial mats, carbonates, methane emissions…) could be observed over the MYKERINOS structure. This feature appears characterized by a chaotic seafloor similar to what was observed more to the East for the Mediterranean Ridge mud diapirs (Huguen *et al*., 2005). Only a few carbonate pavements have been identified, possibly related to an ancient methane venting activity.

Results and discussion

Multibeam data recorded within the Western Nile Deep Sea Fan during the FANIL (2000) and NAUTINIL (2003) cruises evidenced a large number of cone shaped mounds, characterized by high backscatter over their summit area. Detailed *in situ* investigation of three mud cones within a large depression, the MENES Caldera, brings important new results concerning the fluid venting activity of these mounds.

Two of the investigated structures (CHEOPS and CHEFREN) are characterized by a dome shaped morphology, and an important fluid venting activity evidenced over a restricted (200 m in diameter) area located on the summit of the domes and characterized by a high backscatter on the reflectivity maps. Both structures show similar organizations: (1) a central mud/brine expulsion zone, covered nearly continuously by bacterial mats, only locally disturbed by circular black patches interpreted as recent expulsion centers; (2) overflows of this mud/brine mixture out of the central area and accumulation of clear brines along an annular lake at the periphery of the expulsion zone; (3) a transition zone characterized by the scattered presence of thin carbonate pavements, bacterial mats and tube worms at the periphery of the brine lake and (4) light brown pelagic sediments over the mound's slopes. The third structure (MYKERINOS) is characterized by a different morphology, with important depression (crater like) over the summit. No evidence for any type of fluid venting related features (mud/brine flows, bacterial mats, carbonates, methane emissions…) could be identified.

The differences in morphology between the dome-shaped (CHEOPS and CHEFREN) and the crater like (MYKERINOS) structures thus seem to correlate with different fluid venting activity. Two hypotheses can be proposed:

(1) Either MYKERINOS, now inactive in terms of fluid escapes, corresponds to a later stage of evolution compared to the dome-shaped mounds. In this case, the depression observed at the summit of the structure could be interpreted as a previous mud/brine lake, now empty.

(2) Or the two types of mounds are the results of different emplacement processes and thus reveal different fluid dynamics. A diapiric emplacement process can be proposed for MYKERINOS, which is not directly connected to a major fault and a "mud volcano" type emplacement for CHEOPS and CHEFREN.

The mud volcanic provinces of the Gulf of Cadiz Moroccan margin and NW Rif belt: challenging areas to better understand complex marine -land geology at a regional scale

Naima Hamoumi

Department of Earth Sciences, Faculty of Sciences, Mohammed V Agdal University, Rabat, Morocco

ABSTRACT

The Gulf of Cadiz has been the subject of numerous research cruises (TTR9 to 15, CADIPOR I, CADIPOR II, PRIVILEGE MD 140, and PELAGIA), that revealed several mud volcano fields related to fluid venting on the Moroccan margin. They also identified occurrences of carbonate mound structures, cold water corals and carbonate crust in close relationships with mud volcanoes.

On the other hand, sedimentological studies of the flysch domain successions and the external Rif Tanger unit in the NW alpine Rif belt allowed to:

- suggest deposition by argilokinetic processes and fluid circulation during mud volcanoes activity for the poorly sorted Cretaceous to Eocene deposits of Massilyan flyschs and Tanger unit;

- identify the enigmatic *Tubotomaculum* as fossil corals epigenized and coated by Fe and Mn oxides.

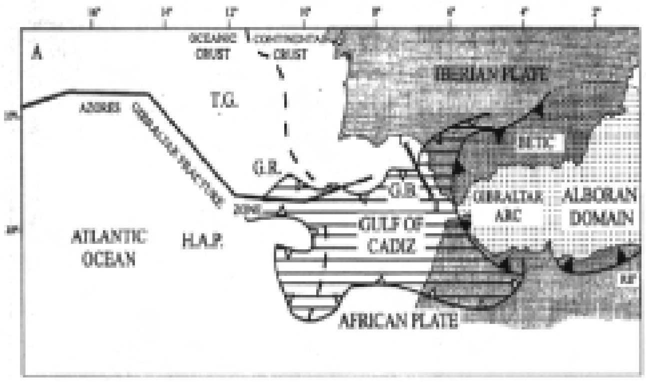
It appears then that more studies must be conducted both offshore and onshore in order to establish the time /space relations between these two mud volcanic provinces and to further understand the regional tectonic evolution and the global and autogenic control.

Key words: Gulf of Cadiz, Moroccan margin, NW Rif belt, Morocco, mud volcanism, carbonate mounds, *Tubotomaculum*.

INTRODUCTION

The peculiarities of the NW Rif belt that correspond to the westernmost part of the Maghrebide alpine belt, are: 1) its connection to the alpine betic cordilleras through the Gibraltar Arc and 2) the offshore extension of its tectono-paleogeographic domains under the Gulf of Cadiz and the Mediterranean Sea.

The Gulf of Cadiz is situated in a tectonically active and extremely complex geological setting (Figure 1). This area is near a major plate boundary characterized by a combination of important strike-slip movement (along the Açores-Gibraltar fracture zone) and compressional tectonics related to the Africa-Eurasia NW-directed convergence. It is also characterized by the presence of an accretionary wedge formed by the westward motion of the front of the Gibraltar Arc during the Middle Miocene (Maldonado *et al*., 1999; Medialdea *et al*., 2004). Since the discovery of mud volcano fields in the Gulf of Cadiz Moroccan margin during research cruise TTR9 (1999), this area has been intensively studied during several research cruises (TTR10, TTR 12, TTR 14, CADIPOR I and PRIVILEGE MD 140), that complemented the previous results by the discovery of new mud volcanoes and occurrences of carbonate mound structures, cold water corals and carbonate crust.



Legend: G.B. = Gaudalquivir Bank; G.R. = Gorringe Bank; H.A.P = Horseshoe Abyssal Plain; T.G. = Tagus Abyssal Plain; △ = Olistostrome front; ▲ = Alboran domain thrust front.

Fig. 1. Regional geodynamic context of the Gulf of Cadiz (modified by Maldonado *et al.*; 1999).

The alpine Rif belt has been a subject of numerous works since 1846 in the framework of mapping or applied geology programs, PhD theses academic research and the linked project across the Strait of Gibraltar. Most of these studies were focused especially on structural studies, geochemistry and petrography, biostratigraphy and geophysics, while sedimentological studies were less developed. Thus the paleogeographical reconstructions and the geological maps proposed for the NW Rifs flysch successions were established without taking into account the sedimentary facies associations and the recent developments in sedimentology and oceanography. Moreover the relationships between the defined tectono-paleogeographic units and their lithostratigraphic content and origin still remain controversial.

Re-examination of the poorly sorted Cretaceous to Eocene deposits, outcropping in Tangers Mountain and Malabata, Sania, Fahs and Sidi Habib areas (Figure 2), suggests deposition by argilokinetic processes and fluid circulation during mud volcanoes activity (Hamoumi, 2000 and work in progress). In addition, study of the enigmatic so called *Tubotomaculum*, identifies them as fossil corals epigenized and coated by Fe and Mn oxides (Hamoumi, 2005). Therefore the NW Moroccan margin appears as a privileged place for increasing our understanding on mud volcanism functioning and associated carbonate build-up as well as the geodynamic evolution of the western Mediterranean alpine belt and the Gulf of Cadiz.

THE OFFSHORE MUD VOLCANIC PROVINCE OF MOROCCAN MARGIN

The existence of mud volcanoes in the Moroccan margin of the Gulf of Cadiz was suspected during the side scan sonar and multibeam bathymetry surveys conducted in 1992 by the Marine Physic Branch of the Naval Research Laboratory (NRL), Washington D.C. in cooperation with the Hawaii Mapping Group and the Naval oceanographic Office.

The data collected during the Leg 2 of TTR 9 survey (1999) from: single channel seismic, 3,5 kHz subbottom profilers, SEAMAP 12 kHz, side scan sonar, seabeam bathymetry, OREtech

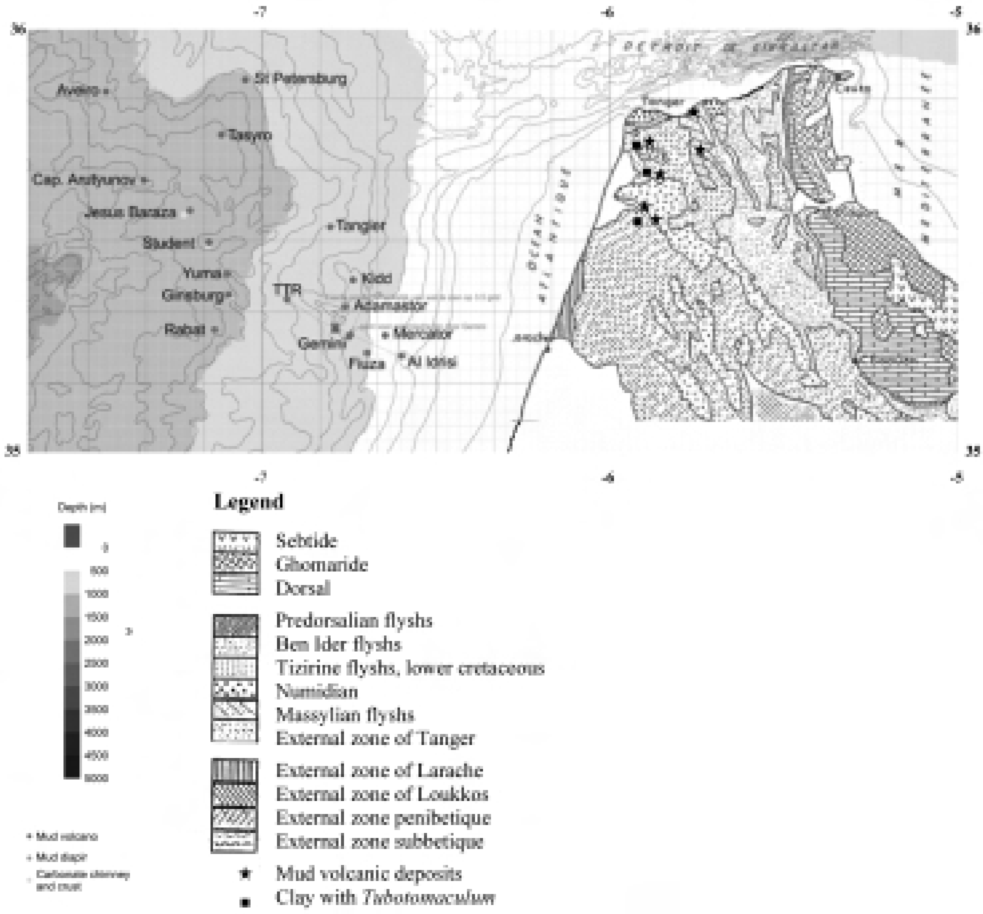


Fig. 2. Location of mud volcanoes and clay with *Tubotomaculum* in Gulf of Cadiz Moroccan margin and NW Rif belt.

side scan sonar, coring, dredging and video imaging, confirmed this hypothesis and allowed the discovery of three mud volcano fields related with venting of fluids oversaturated in methane: the Western Moroccan Field (WMF), the Middle Moroccan Field (MMF) and the Eastern Moroccan Field (EMF). The mud volcanoes are conical in shape with diameter ranging from several tens of meters to 4 km and heights up to 200 m. In the most active mud volcanoes of the MMF hydrocarbon fluid escape, methane clathrates, chemosynthetic organisms and authigenic carbonates have been recovered (Kenyon *et al*., 2000b; Gardner, 2001).

Since 2000, the Gulf of Cadiz Moroccan margin has been intensively studied during several research cruises: TTR 10 (2000), TTR 12 (2002), CADIPOR I (2002) and TTR14 (2004). These research cruises complemented the previous results by the discovery of new mud volcanoes related to fluid venting in the previously identified fields and a new mud volcano field (Figure 2): the Al Arraich field that consists of eight mud volcanoes up to 255 m high and 5.4 km wide, located at water depths between 700 and 200 m, (Van Rensbergen *et al*., 2005b; Kenyon *et al*., 2002b; Akhmanov *et al*., 2003; Pinheiro *et al*., 2003a). They also identified:

- cold seep communities (the most common species are the pogonophoran worm *Siboglinum* sp. and the solemyid bivalve *Acharax* sp.) especially in mud volcanoes showing evidence of relatively recent seepage activity in the Moroccan fields (Rodrigues and Cunha, 2005);

- deep-sea coral reefs associated with giant mud volcanoes at depths between 200 and 800 m in the Larache offshore (Van Rensbergen *et al*., 2005b);

- fragments of dead corals (*Madrepora* and *Lophelia*) and carbonate crusts.

The discovery of juvenile carbonate mound structures and mud volcanoes with cold water corals, gaz hydrates and carbonate crusts has integrated this part of the Moroccan margin in several European and international projects (ESF Euromargins, EU FP6, UNESCO IOC) and research surveys: PRIVILEGE MD 140 (2004), CADIPOR II (2005) and PELAGIA (2005).

Most of the mud volcanoes have been sampled, mud breccias recovered and clasts studied. X-ray mineralogical study revealed that the mud breccias are characterized by the clay mineral assemblage: smectite, kaolinite and chlorite (Kenyon *et al*., 2000b; Hamoumi *et al*., 2005). Such mineralogical composition is known in the Eocene and Oligo-Miocene successions of the Rif belt. However the high smectite and kaolinite contents reflect the existence of authigenic smectite and kaolinite related to the alteration processes during the mud volcano activity.

Study under polarizing microscope of thin sections of mud breccias rock clasts collected by a TV-grab sampler lead to the recognition of four main groups of rocks that are known in the geological formations of the Rif belt: volcanic rocks (porphyritic basalt); volcanoclastic rocks; limestones (biomicrite, biomicrite with stromatolites, sparititic limestone, bioclastic limestone) and mixed siliciclastic/carbonate rocks (silty biomicrite, sandy biomicrite, sandy allochemic limestone, muddy bioclastic limestone) (Rachidi *et al*., 2003; Hamoumi *et al*., 2005).

Dating based on calcareous nannofossil assemblages and plankton foraminifers of mud volcano rock fragments indicate Eocene and Miocene ages (Sadekov and Ovsyannikov, 2000; Barvalina and Sarantsev, 2004).

THE NW RIF BELT INACTIVE MUD VOLCANIC PROVINCE

The onshore mud volcanoes

The western part of the northwestern alpine Rif belt (Figure 2) consists of Mesozoic to paleogenene allochtonous nappe complexes (flysch domain): The Numidian, Beni ider and Massylian flyschs that overlie the external Rif Tanger unit (Durand Delga, 1993; Suter, 1980; Hoyez, 1989).

The Melloussa nappe belongs to the Massylian flyschs (Durand Delga, 1965). It is composed of Albo Aptian silisiclastic flysch overlain by Upper Cretaceous (Cenamonian Thuronian) limestones and mudstones (Gubeli, 1982; Thurrow, 1987). The Tanger unit (Intrarif), that belongs to the external Rif (Durand Delga and Mattauer, 1959) crops out widely in the NW Rif and appears as isolated tectonic blocs associated with strike slip faults, exhibiting various facies and various thicknesses (Lespinasse, 1975). The most representative succession consists of marlstone and mudstones that can reach more than 600 m in thickness, overlain by a cover composed of Eocene cherty limestone and aquitanian alternating marlstones and sandstones turbiditic succession. (SNED and SECEG, 1990). The chaotic succession of Melloussa and Tanger units was interpreted as: 1) a Miocene olistostrome (“argile à blocs”), realized from the disintegration of the flyschs (Bourgois, 1978), 2) superficial solieflucted deposits (Durand Delga, 1993) and 3) gravity flow deposits emplaced by gravity sliding and slumping (Hamoumi, 1995) in the talus of a delta slope system (Hamoumi *et al*., 1995).

Re-examination of Melloussa nappe and Tanger unit chaotic deposits outcropping in Tangiers Mountain and Malabata (subsurface and surface), Sania, Fahs and Sidi Habib areas, on the light of the new oceanographic discoveries and by using geomorphology, facies analysis, sedimentary petrology, mineralogy and geochemistry, allows to identify onshore mud volcanic deposits (Hamoumi, 2000 and work in progress). Deposition by argilokinetic processes and fluid circulation and expulsion during a mud volcano activity is confirmed by the discovery of gas (methane) during drilling in GEO3 at 147 m and SB5 at 180 m (in Durand Delga, 1993) and by the low chlorine water in the Malabata well (Chraibi *et al*., 1995).

Morphology and organization

The ten mud volcanoes identified in Tangers Mountain and Malabata, Sania, Fahs and Sidi Habib areas are conical in shape with diameter ranging from several tens of meters to 4, 5 km and heights reaching 481 m. They are aligned according to two preferred trends: NW-SE and NE-SE and some of them are overlain by numidian deltaic successions.

Sedimentological evidence

These deposits correspond to a mixture of red, green and grey clay and/or marl matrix including clasts that vary in size (millimeter to hectometer scale), shape (rounded to angular) and lithology (red mudstones, green, mudstone, grey mudstone, silty mudstones, siltstone, calcareous sandstone, calcarenite, calcareous siltstone, limestones). Moreover, they exhibit the typical composition, texture, features and structures of a mud volcanic deposit as follow:

- the presence of several kinds of clays (gray, greenish, green and red clay) in the matrix that can be sometimes mixed in the same level;

- the aspect of the matrix clays: crumbly texture, glossy shard like fragments showing micro shearing, calcareous fragments and soft sediments deformations;

- the co-existence of polygenic clasts: 1) brown concretions, 2) crystalloclasts, gravels, pebbles and blocs realized from the disintegration of old deposits known to be from the the Rif chain successions, 3) clasts realized during hydrates precipitation such as polymictic clasts (composed of red clay matrix and angular calcareous fragments, of splintery clay matrix and siltstones gravels, or of sandstone pebble coated with massive clay), structureless limestone clasts with calcareous veins and poorly consolidated siltstone or mudstone clasts;

- the lack of grading and often of preferred orientation;

- the existence of levels with lenticular bedded structures;

- the mixture of sediments of different ages (Lower Cretaceous, Upper Cretaceous, Eocene Oligo – Miocene, Miocene);

- the degree of the weathering maturity of the sediments;

- the existence of authigenic minerals: smectite, vermiculite, calcite and pyrite;

- the chemical changes (alteration, dissolution and recrystallization) and the breakage that affect the microfossils;

- the existence of organic matter-rich levels.

The fossil records (*Tubotomaculum*) of coral build-ups

The *Tubotomaculum* occurs in the upper Cretaceous to Miocene argillaceous formation (“argile varicolore”) at the base of the Numidian flysch successions in the western peri-Mediterranean alpine orogenic belt. They have been considered for a long time as enigmatic geological bodies and there were many controversial hypotheses about their origin and mode of genesis: epigenous burrows and coprolite (Durand Delga, 1955), epigenous burrows for the cylindrical shape and, fecal pellets, mud fragments, authigenic iron grains or particular concretions of manganese and iron oxides (Pautot *et al*., 1975).

In the western Rift belt of Morocco, the *Tubotomaculum* occurs in the under numidian varicoloured clays (“argiles à *Tubotomaculum*”) that lie at the top of mud volcanic deposits (Figures 2 and 3). These under numidian successions correspond to the prodelta of the wave, storm and /or tide influenced numidian delta system of Oligo Miocene age (Hamoumi *et al*., 1995). Sedimentological study of these *Tubotomaculum* using macroscopic (visual) description, petrologic and mineralogical studies (thin and polished section), X-ray diffraction on bulk sediment and chemical analysis, allows their identification for the first time as fossil corals epigenized and coated by Fe and Mn oxides (Hamoumi, 2005).

These *Tubotomaculum* are dark brown to black ferromanganese bodies composed of a core and a bumpy cortex. Their sizes range from 1 to 4 cm in diameter and 2 cm to 10 cm in length. They can be assigned to various shape classes: conical, trochoidal, pyramidal cylindrical, twisted, dendroid and irregular that may be compared to the morphology of some *scleratinia*. Their cortex displays several successive dark brown or black layers and they exhibit morphological structures that characterize coral skeleton such as: corallites, septa, dissepiments and rounded septal dentations.

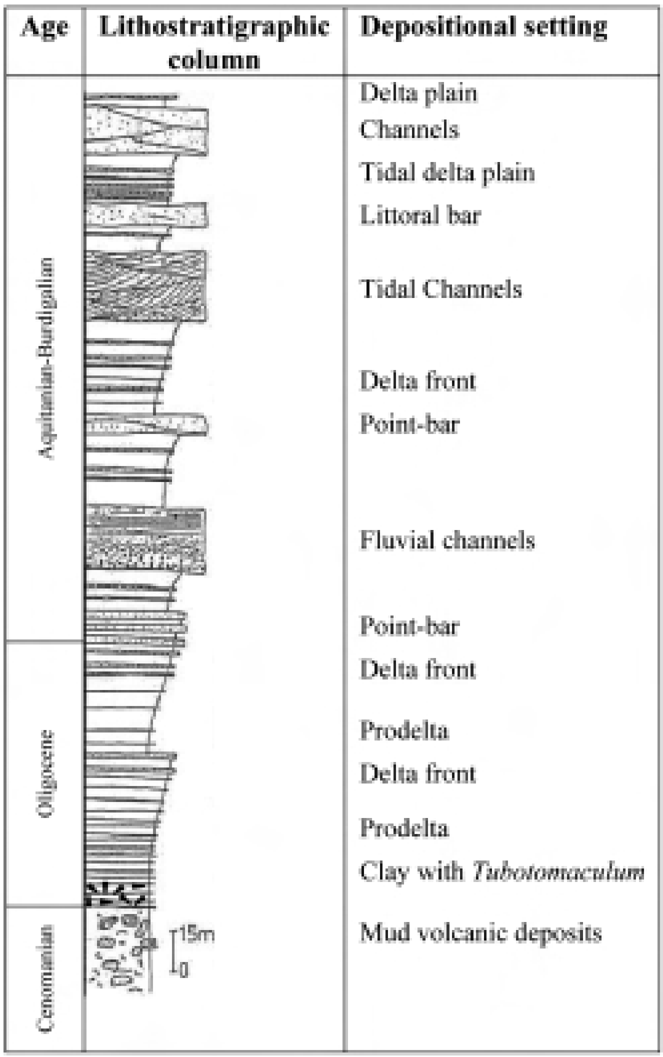


Fig. 3. Ziaten succession.

X-ray diffraction revealed the manganite together with goethite and hematite in the cortex and goethite in the core and the peripheral layer of the cortex. Chemical analyses using spectrometry show significant difference among the core and the cortex, the highest concentration of Mn is located in the cortex (13, 2%), the core has low concentrations: 8% and 6, 40%. While Fe content follows an inverse trend, the highest concentrations are located in the core (36% and 35, 32%) and the cortex displays lower value (30, 68%).

Such encrustations form during a long and complex diagenetic evolution under the combination of autogenic and allogenic factors. The authigene ankerite and calcite recognized by Kozlova *et al*. (2005) in the dead corals collected in the Gulf of Cadiz, may correspond to an early stage of the diagenetic evolution of these fossil corals epigenized and coated by Fe and Mn oxides.

Conclusion and recommendations

The Moroccan margin of the Gulf of Cadiz has been intensively studied between 1999 and 2004 and mud volcanoes and associated deep-water reef-like coral build-ups have been documented, sampled and described. Nevertheless, there is still questions on 1) the geodynamic evolution of the Gulf of Cadiz, 2) the allogenic and autogenic control of mud volcanoes and carbonate mound, 3) the linkage of carbonate build ups to (hydrocarbon related) cold seeps, 4) the lithology and age of all the geological formations reworked by the mud volcanoes. The discovery of mud volcano outcrops in the NW Rif belt indicates that this phenomenon was probably initiated during

Miocene times and must be integrated in the regional tectonic history of the alpine Rif belt. The association of mud volcano deposits with manganese coated fossil corals is an additional argument for a linkage between mud volcanism and carbonate build ups.

Thus, the Gulf of Cadiz active mud volcanic province and the NW Rif Belt inactive mud volcanic province appear as critical places to better understand all these phenomena. In addition the discovery of mud volcano in the marine domains of many regions of the world and the numerous data obtained offer us a new genetic model for poorly sorted sediments that are interpreted usually by gravity flow processes. It is necessary than to take into account this important phenomenon when interpreting ancient deposits.

Consequently, much more research is needed in the Gulf of Cadiz and at the same time, more detailed studies must be conducted onshore on the geological formation of the North Western Rif belt (mapping, sedimentology, biostratigraphy) in order to:

- define the extent, the age and the geodynamic context of the mud volcanism phemenon;

- precise the relationship between 1) offshore and onshore recent and ancient mud volcanoes 2) mud volcanoes, carbonate mounds and carbonate crust and 3) *Tubotomaculum* and mud volcanoes;

- compare the petrographical and mineralogical composition and paleontological data of the offshore and onshore mud volcano clasts and matrix with those of the geological formation of the Rif chain;

- better understand the structural organization of the Moroccan margin subsurface;

- better document the alteration processes associated with mud volcano activity;

- establish a new genetic model for poorly sorted sediments that are interpreted usually by gravity flow processes.

The examination of the gas hydrates hosting environment of the Anaximander mud volcanoes, Eastern Mediterranean: stratigraphy and sedimentary succession o f the mud breccia clasts

Chr. Ioakim[1], St. Tsaila-Monopolis[2], C. Perissoratis[1], V. Lykousis[3] and the Anaximander scientific party

[1] *Institute of Geology and Mineral Exploration, Athens, Greece*
[2] *University of Patras, Rio, Greece*
[3] *Hellenic Center of Marine Research, Mavro Lithari, Anavyssos, Greece*

ABSTRACT

Box and gravity cores were collected in the Eastern Mediterranean Mud Volcanoes (MVs), during May 2003 and October/November 2004 cruises of the R/V *Aegaeo* carried out in the framework of the EU funded "Anaximander" project. The target of this project is the examination of the Gas Hydrates (GH) hosting environment and the associated deep biosphere occurring at the Anaximander Mountains (Mts), Eastern Mediterranean. In the mud volcanoes a sorted matrix-supported breccia was found, containing rock clasts derived from the deeper formations which provided information for the rock sequences that underlie the mud volcanoes. The petrography and biostratigraphy of the mud breccia clasts from Amsterdam, Kazan, Kula, Athina and Thessaloniki MVs helped in outlining the deep stratigraphy of the area contributing to a better understanding of the formation and geological evolution of the Anaximander Mts.

Key-words: mud volcanism, Eastern Mediterranean, palaeoenvironment, mud breccia rock clasts, Cretaceous-Tertiary.

1. INTRODUCTION

For over 20 years the Eastern Mediterranean mud volcanoes has been the focus of a number of multidisciplinary investigations (Cita *et al.*, 1981, 1996; Staffini *et al.*, 1993; Limonov *et al.*, 1996; Woodside *et al.*, 1998; Kopf *et al.*, 2000; Akhmanov, 1996; Akhmanov *et al.*, 2003; Charlou *et al.*, 2003; Daehlmann *et al.*, 2005; de Lange and Brumsack, 1998; Emeis *et al.*, 1996; Foucher *et al.*, 1999; Lykousis *et al.*, 2003, 2004; Perissoratis *et al.*, 1998, 2003; Robertson *et al.*, 1996a; Salas and Woodside, 2002; Zitter *et al.*, 2003; Ten Veen *et al.*, 2004).

Mud volcanoes, which result from the extrusion of fluid rich mudflows (mud breccias), are often associated with methane seepage and gas hydrates formed under appropriate pressure and temperature conditions (Milkov, 2000; Werne *et al.*, 2004). According to many authors (e.g. Yassir, 1989; Kopf *et al.*, 2000) the mud volcanic activity is a well known phenomenon in areas undergoing collision tectonics.

Moreover, the presence of mud domes along parts of the Mediterranean Ridge Complex and especially those of the Anaximander Mts (Figure 1), is related to the collision between the African and Eurasian plates, causing backthrusts along which mud ascends and extrudes (Mascle *et al.*, 1999; Kopf *et al.*, 2000). Mud volcanoes are believed to play a major role in the fluid and gas budget and in the geochemical cycle within the subduction zone. The Anaximander Mts complex, located offshore of southwest Turkey between Rhodes and Cyprus; constitutes an important link between the Hellenic and Cyprus Arcs (Zitter *et al.*, 2003; Ten Veen *et al.*, 2004). In particular during the initial stages of continental collision in the Eastern Mediterranean, this area played a key role in the triple subduction between the African and Eurasian and the Anatolian microplate. This plate boundary is well defined through the Hellenic Arc to the west and through the Cyprus Arc to the east. The occurrence of mud volcanism, cold seepage hydrocarbon venting and gas hydrates in the Anaximander area has been intensively investigated since 1991 in the framework of various international projects (MEDINAUT/MEDINETH, ANAXIPROBE/TTR Training-Through Research programs).

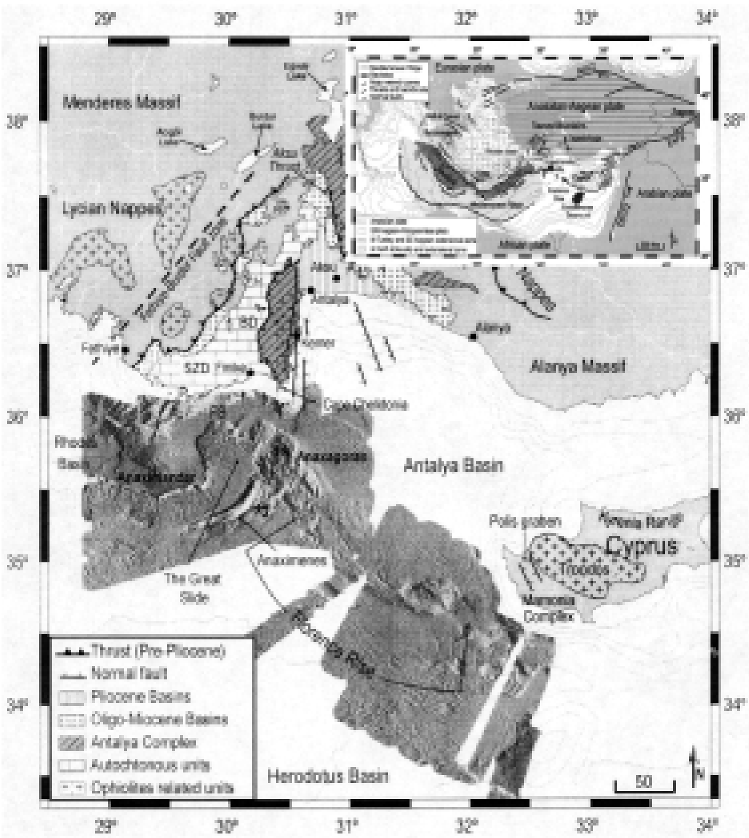


Fig. **1.** Outline geological map of the main stratigraphic units of the studied area (presented by Zitter *et al.*, 2004).

Within the framework of the EU project ANAXIMANDER in (2003 – 2005) new research was carried out, to focus on further investigations of this earlier mapped area. The principal objectives of the project are:

a) to investigate the nature of acoustic backscattering by correlating the sedimentary facies and their geophysical features, b) to proceed to the collection of undisturbed sediments using autoclave cores without dissociating the gas hydrates and keeping the *in situ* conditions, c) to study the sediments, their depositional environments and the associated deep biosphere and d) to link all processes associated with fluid flow such as the biological and the geochemical activity present at the mud volcanoes and combining all above results, in order to present a picture as comprehensive as possible of this extreme environment.

The detailed geological exploration was carried out during two cruises of R/V *Aegaeo*, in May 2003 and October/November 2004, providing ample new data and confirming that the Anaximander Mts is an important site for studying the active mud volcanism and gas hydrates formation. This research led to the discovery of two new mud volcanoes named Athina (Lykousis *et al*., 2004) and Thessaloniki. In particular, the mud breccia recovered from all mud volcanoes (Amsterdam, Kazan, Kula, Athina and Thessaloniki) contained numerous clasts from the deep seated strata of Anaximander Mts (Figure 2). In these sites an extensive sampling of mud breccia clasts was realized in both expeditions, where a total of 67 sediment gravity cores, 17 box – cores and 6 autoclave cores were retrieved at the targeted sites.

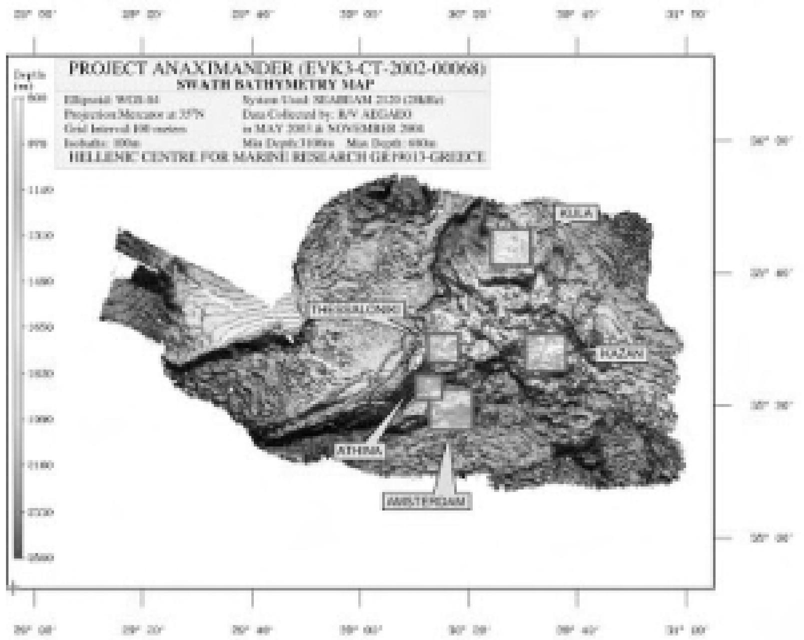


Fig. **2.** Generalized geotectonic and bathymetric map of the Eastern Mediterranean. Relative location of the Anaximander Mountains is indicated (presented by Lykousis *et al.,* 2004).

The main aim of this paper is to report results from the petrographical and micropalaeontological studies of the clasts and the matrix of the prenoted mud volcanic sediments, in order to use these informations for the re-interpretation of the depositional setting and the geological evolution of the Anaximander area preceeding the mud volcanic activity.

2. MATERIAL AND METHODS

Generally the mud breccia from the different sites are gray and greenish gray in color, with sandy and silty admixture, matrix-supported, with a large quantity of angular or subangular rock fragments of different size and origin. Various sandstones, claystones, mudstone are the predominant lithologies, in the rock clasts from the mud breccia. Each mud breccia flow usually is structureless with stiff or a soupy feature and it is gas saturated in certain sites characterized by a strong smell of methane and hydrogen sulfite.

Every collected rock clast was described in detail and clasts with similar characteristic (composition, structure and texture) were grouped together. Thin sections from the different groups were identified and analyzed under a polarized microscope. The main genetic indicators of all clasts were examined in order to determine the depositional processes, their age and their environment during deposition. A petrographical – micropalaeontological study of 120 samples of mud breccia clasts from the mud volcanoes of the Anaximander Mts was carried out provide a tentative reconstruction of the sedimentary sequence in the Anaximander Mts (Figure 2).

Sampling sites

Specifically the location of the clasts examined and the sampling were as follows:

Amsterdam MV: a series of 30 box and gravity and two autoclave cores were recovered. Most of the sediment cores were retrieved from the central mound which appears to be the most recent volcanic activity, containing crystals of gas hydrates. The sediments consist of a gray/olive gray mud breccia characterized by a soupy or stiff feature as containing rock clasts of 0.2 – 12 cm in length. A high content of clay and silt ranging between 55-65% and 15-30% with a percentage of sand about 12% was found. Only two of the gravity cores taken from the outer slope recovered a gray clay hemi pelagic sediments intercalated with sapropelic layers.

Kazan MV: twenty cores (17 gravity and 3 box and one autoclave cores) were retrieved from Kazan. In this MV gas hydrates were found and appeared as rice-like lumps, rather regularly dispersed throughout the sediment matrix was retrieved. Only one box core containing hemi pelagic sediments. The mud breccia was highly saturated in gas and contained many fragments of soft sediments and clasts up to 5-7 cm in size.

Kula MV: a series of 23 gravity and 4 box cores were taken containing both hemipelagic and typical mud volcano breccia texture. In particular most of the cores retrieved from Kula MV have a typical hemipelagic vertical sedimentary sequence with sapropelic layers overlying by at thick oxidized layers. High amounts of mud breccia contained clasts of different size and origin ranging from 0.5 to 4 cm in length like mudstones and ophiolitic materials (fragments of serpentine and serpentinized-peridotite).

Athina MV: four gravity cores were recovered from the summits of this northward-located mound. A typical mud breccia was sampled with a grayish matrix supporting angular subangular clasts of mudstones and size ranging from 0.5-3 cm in length. The soupy structure with high amounts of water is indicative of gas hydrates dissociation.

Thessaloniki MV: four gravity cores were recovered from, the mud breccia characterized by textures indicating active mud volcanism (mud breccia, presence of gas hydrates crystals, dissociation features. The cores contained a soupy mud breccia with very high water content and negligible amounts of mud rock clasts.

3. Sedimentary structure-age

The main sedimentary groups identified on the basis of their lithology and their age are: mudstones 60%, sandstones/siltstones 10%, limestones 25%, and ophiolitic materials 5%, which were the representative percentages for 120 rock clasts. The petrographical–facies analyses under polarized microscope led to further subdivisions of the groups. The age of these lithological groups range from Upper Cretaceous to Middle/Upper Miocene; the defined groups are described (Plate 1-3):

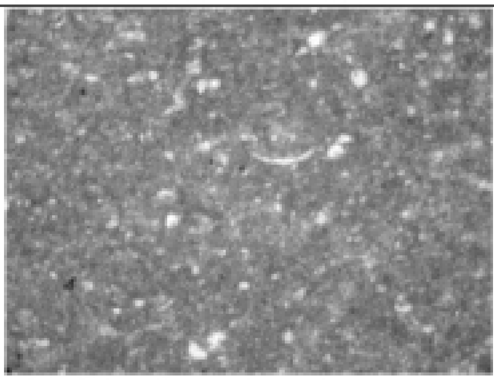
3.1. Limestones group

Recrystallized fossiliferous micrites (F1): white or gray light in color structureless with sporadic recrystallized foraminifera (fragments or unbroken tests) filled by crystalline calcite, of Late Cretaceous age (Globigerinidae, *Hedbegella* sp., *Rotalipora* sp.). They were collected from Kula and partially from Kazan MVs. Few rock clasts, whitish in color and massive, angular to subangular, 2-3 cm in size, composed mainly by sporadic recrystallized pelagic foraminifera supported by microcrystalline calcite, aggregate calcite and a complex system of calcite veins, were collected from Amsterdam MV of Late Cretaceous age.

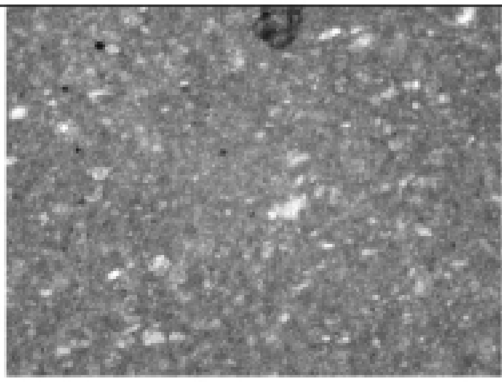
Fossiliferous micrites (F2): gray light in color, consolided composed mainly of well preserved pelagic foraminiferal (10-60%) supported by micritic calcite. The foraminiferal assemblages are

AN07BC1, AN06BC1

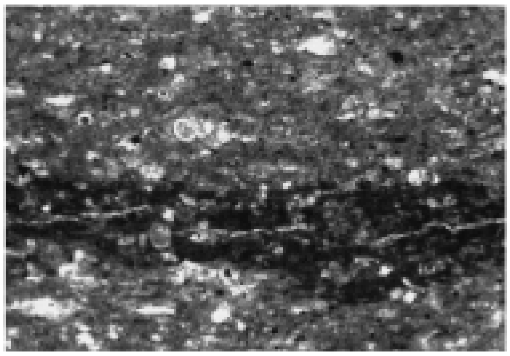
Kazan mud volcano clast



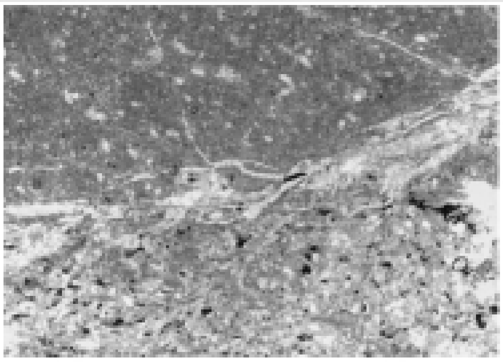
AN07BC1-1



AN07BC1-2

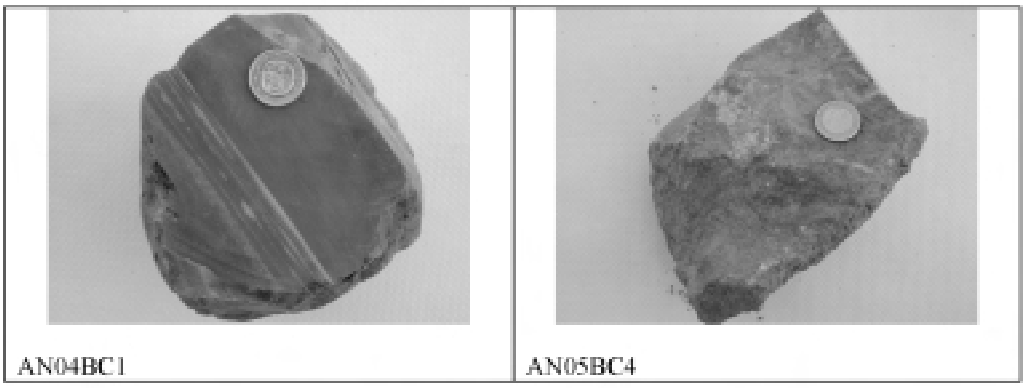


AN06BC1-1



AN06BC1-2

Plate 1. AN07BC1-1 micritic limestones with foraminifera; AN07BC1-2 micritic limestones with foraminifera; AN06BC1-1 intercalation of mudstone with carbonate cement and clay - stone with planktonic foraminifera; AN06BC1-2 Fossiliferous micrite with cross veins of calcite.



Amsterdam mud volcano clasts

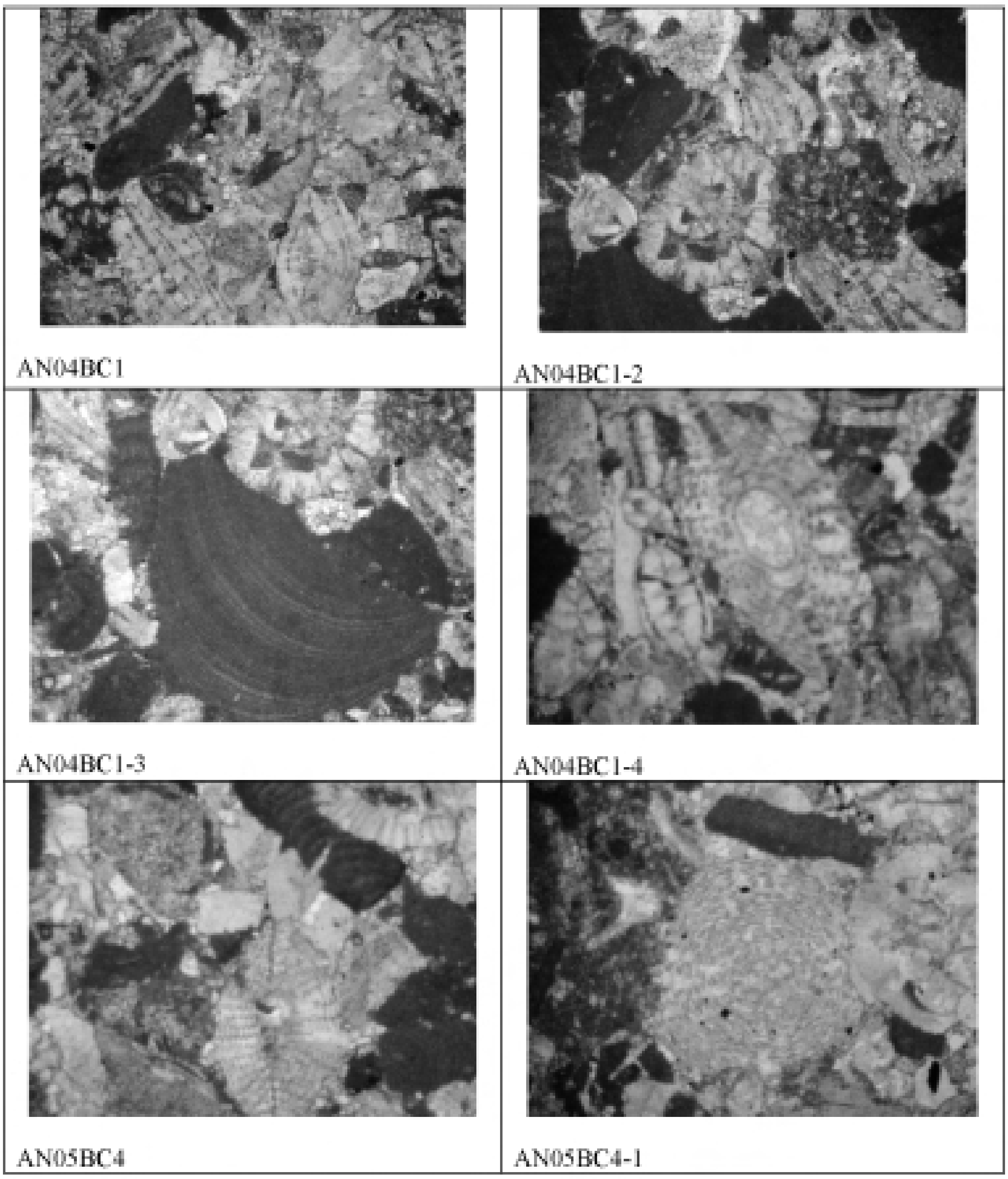


Plate 2. Microfacies from mud breccia clasts Amsterdam MV. ANO4BC1, AN04BC1-2, AN04BC1-3, AN04BC1-4, AN05BC4, AN05BC4-1 Bioclastic limestones with benthic and planktonic foraminifera (*Nummulites intermedius,* Rotaliidae, *Lepidocyclina* sp.*, Sphaeogypsina, Fabiania* sp., algae of Melobesoidae).

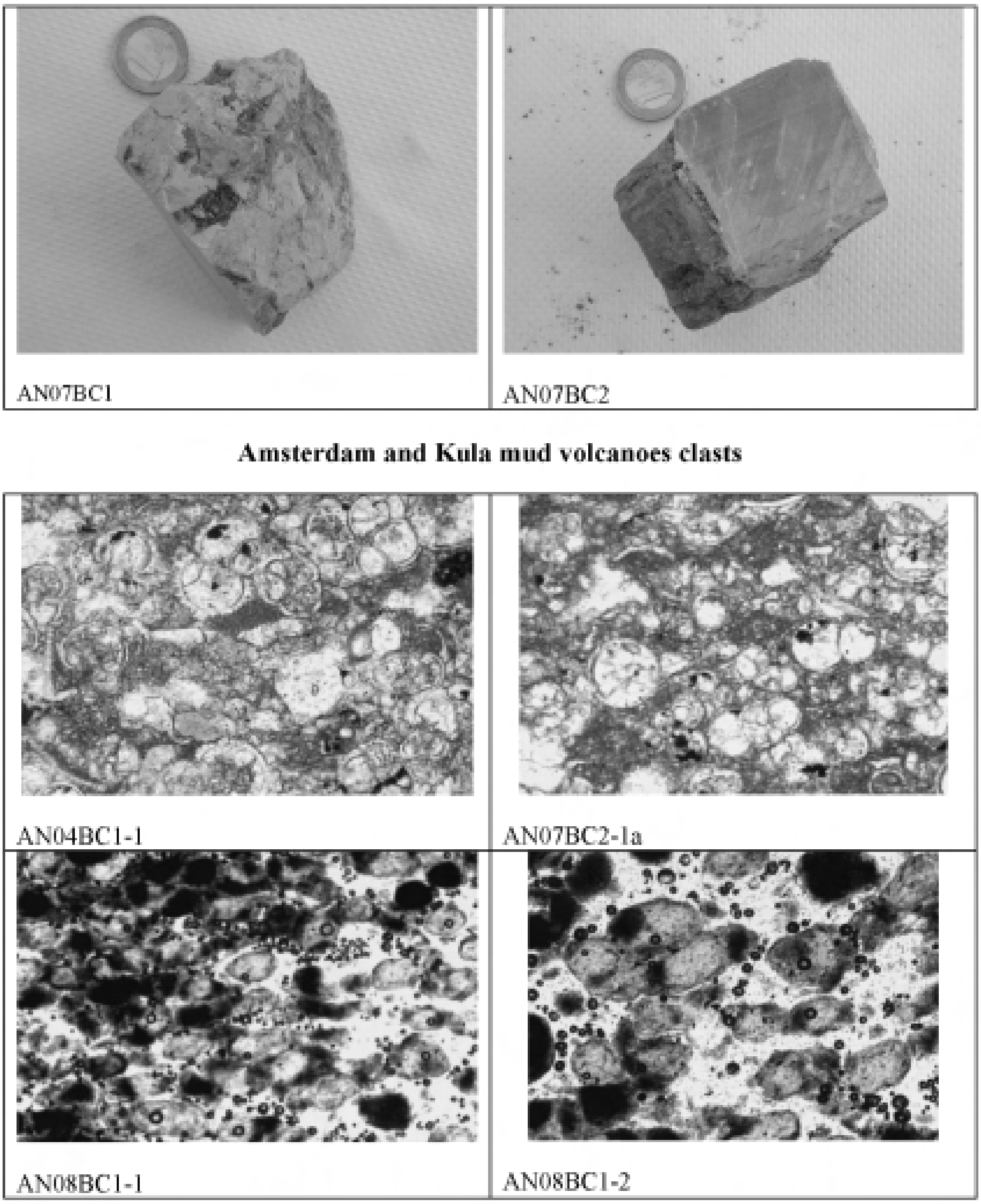


Plate 3. AN04BC1-1 Calcareous mudstone with planktonic foraminifera; AN07BC1-2 Calcareous mudstone with planktonic foraminifera; AN08BC1-1 Subquartzose siltistone rich in organic detritus with planktonic foraminifera; AN08BC1-1 Subquartzose siltistone rich in organic detritus with planktonic foraminifera.

very small in size, their chambers filled usually by sparitic calcite or by pyrite of Lower-Middle Miocene age *(Orbulina universa, Globigerinoides trilobus, Globigerinoides* sp., *Globoquadrina dehiscens*). The preservation of the pelagic organisms imply sedimentation in open sea and calm conditions. The rock clasts have been collected from all mud volcanoes.

Detrital biomicrites (F3): light gray in color mainly composed of planktonic foraminifera and fragments, fine grained aggregates of calcite, silty sized angular quartz grains supported by a micritic calcite matrix. Bioclasts are prevalent among the detrital components. A clayey and organic admixture is observed. Fine calcite crystals and pyrite framboids occur as minor components. The preservation of the pelagic organisms implies sedimentation in open marine environments. Foraminiferal assemblages indicate a Middle/Upper Miocene age *(Orbulina universa, Orbulina suturalis, Globigerinoides trilobus, Globoquadrina dehiscens*).

Biocalcarenites (F4): dark gray in color, the detrital components are polymictic, but mainly consisting of biogenic components (65%). A great variety of benthic foraminifera was observed (*Nummulites intermedius, Lepidocyclina* sp., *Operculina* sp., *Amphistegina* sp., Rotaliidae, algae of Melobesoideae, debris of Lamellibranchs and Echinoderms) indicating an Oligocene age. Biodetrital components often observed imply a redeposition from pre-existing limestones (*Nummulites* gr. *laevigatus, Gyroidinella magna, Shraerogypsina* sp., *Discocyclina* sp., Rotaliidae, *Operculina* sp., *Fabiania* sp., Globigerinidae, algae of Melobesoideae, debris of Lamellibranchs and Echinoderms). Their polymicritic composition, the important contents of terrigenous material, inclusions of lens – like detrital biomicrites and a large amount of shallow water organisms, suggest that these rocks were deposited in an active hydrodynamic environment of a shelf area. They have been collected from Amsterdam MV.

3.2. Sandstone and siltstone group

Subquartzose arenites (K1): gray in color, massive, fine to medium grained and indurated. The sandstones are predominantly composed of subangular quartz grain (55-60%). Other secondary constituent are glauconite, fine grained K-feldspar biotite and fine grained micrite fragments. Rare reworked pelagic foraminifera of Late Cretaceous were observed. These rocks were found mainly in Kula and secondly in Kazan MV.

Siltstone (K2): gray in color, with planar cross lamination observed; the siltstone are mainly composed of subangular quartz grains, glauconite grains, feldspar, biotite and rare small-size planktonic foraminifera with chambers filled by calcite. Pyrite framboids and organic detritus are very abundant, a few reworked Late Cretaceous and Palaeocene species were found with rare planktonic foraminifera. They are characterized by horizontal laminations, important contents of microslumping and bioturbation. These indicators suggest a turbiditic origin. This lithotype of siliciclastic rocks was found in abundance in Kula and Kazan MVs.

3.3. Mudstone group

Mudstones (L1): light gray thin planar laminated indurated, found among mud breccia clasts from all mud volcanoes, composed mainly of clayey, probably chlorite-illitic matrix with a silty admixture of fine angular-subangular quartz grains fine sized aggregates of chalcedony mica, organic detritus. Pyrite and authigenic calcite occur in abundance. The lithotype contains a rich microfauna of pelagic foraminifera *(Orbulina universa, Globigerinoides trilobus, Globoquadrina dehiscens*) indicating a Miocene age. They were collected from all mud volcanoes.

Another lithotype is the ***calcareous mudstone (L2)*** which was observed from all MVs. Light gray and massive clayey. It is polymictic, matrix – supported, composed mainly of planktonic and sporadic benthic foraminifera, very fine grained subangular quartz silty sized angular volcanic glass and organic detritus in a clayey illitic matrix. Minor grains are feldspars, glauconite, fragments of micrite and fragments of fossiliferous limestone pyrite, gypsum and anthigenic calcite occur in the rock. The micropalaeontological study indicates a Middle/Upper Miocene age of these rocks deposited in a relative calm water marine environment *(Orbulina universa, Orbulina suturalis, Globigerinoides trilobus, Globoquadrina dehiscens*).

Finally, the mud breccia contained also few rock clasts of ophiolitic material (fragments of serpentine and serpentinized peridotite) that were collected from Kula and Kazan MVs.

4. Interpretation - Discussion

The mud volcanoes in the Anaximander Mts erupted a poorly sorted matrix-supported breccia, containing rock clasts derived from lower lying formations bed. The morphology, petrography and biostratigraphy of the mud breccia clasts from Amsterdam, Kazan, Kula, Athina and Thessaloniki MVs thus helped in outlying the deep stratigraphy and hence a better understanding of the formation and geological evolution of the Anaximander mud volcanoes. Also microfacies analyses (forams), carried out in thin sections through microscope, and X-ray diffraction analyses, resulted in a more precise estimation of the relative age of the source rock formations and a subsequent determination of the depositional environment during rock formation.

A large variety of types were described among the mud breccia clasts from each mud volcano, through the macro-microscopical analyses, which were classified as follows: recrystallized fossiliferous micrite, fossiliferous micrite and detrital biomicrite, sandstone and siltstone enriched in organic detritus, biocalcarenite, mudstone and calcareous mudstone. The dating of these rock fragments indicates in a vertical sedimentary sequence; a Late Cretaceous limestones, overlaid by Paleocene siliciclastic rocks, followed by Eocene biogenic limestones and finally by Miocene mudstones. The results presented suggest that the palaeogeographic context largely varies between the eastern and the western parts of Anaximander Mts, as is clearly indicated by the differences in the geology of the two regions.

The eastern part (Kula and Kazan MVs) represented at least during the Upper Cretaceous, an area where carbonate pelagic sediments were deposited, followed by a large amount of green – gray siliciclastic imputs that were typical of the allochthonous series of Antalya Nappes complex (i.e. ophiolitic material). During the Paleogene time, a regression led to the deposition of important siliciclasts series. This interpretation agrees well with the hypothesis of Robertson (1998) and Akhmanov *et al.* (2003) concerning the regional tectonic re-arrangement of Neotethyan basins in eastern Mediterranean. A transgressive system was widely developed in this area during the Miocene with a prevailing carbonate pelagic sedimentation. This conclusion is in agreement with the sedimentary evolution of the Antalya Nappes, presented by Bernoulli *et al.*, 1967; Huguen *et al.*, 2002; Woodside *et al.*, 1998, 2000; Zitter *et al.*, 2003; Ten Veen *et al.*, 2004.

According to the present results, in the western part of the Anaximander mountains (Anaximenes and Anaximander Mts), a deep marine environment also was present at least since the Upper Cretaceous. The fact that the Paleocene sediments are missing from the sampling sites of Amsterdam MV probably indicates local uplift movements and a non-deposition or erosion of the surface of sediments.

During the Eocene – Oligocene a shallow environment already existed as shown by the deposition of neritic limestones, similar to those found in the autocthonous series of Bay Daglari and Susuz Dag., overlaid by important transgressive accumulations attributed to the Miocene. In contrast, the absence of paleocene sediments is probably due to the uplift of the area and non-deposition or erosion of the surface or lack of sampling material.

These results again indicate similarities to those recorded in the outcropping of Kastelorizo and Ro Islands, northeastern of Anaximander Mts (Galeos, 1986), based on the same faunistic associations and dated of Upper Cretaceous to Miocene age. Also the above mentioned fauna included in the clasts, is similar to that of outcropping in Southern Turkey Daglari Bay and Susuz Dag (Bernoulli *et al.*, 1974; Woodside *et al.*, 1998, 2002).

5. Conclusion

A stratigraphy of the Anaximander Mts has been inferred from the study of rock clasts, collected from the five mud volcanoes. Eight principal rock types were recognized in to three sedimentary groups. The diversity in rock types and age demonstrates a complex stratigraphy for the sedimentary succession of the Anaximander area. The age of the rock clasts varies from Upper Cretaceous to Late Miocene. The results suggest that the palaeogeography of the area varies between the eastern and the western parts of Anaximander Mts, as clearly indicated by the differences in the geology of the two regions. Finally, it can be concluded that the western mountains belong to the Eastern Hellenic Arc (Preapulian zone) deformation (Woodside *et al*., 2000), while the eastern mountains (Kula and Kazan MVs, Anaxagoras seamount) form the western limp of Cyprus Arc. (Woodside *et al*., 1998; Zitter *et al*., 2003; Ten Veen *et al*., 2004).

Acknowledgements

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Methane-related carbonates and associated authigenic minerals from the Eastern Mediterranean Sea

S. Gontharet[1], C. Pierre[1], M.M. Blanc-Valleron[2], J.M. Rouchy[2], Y. Fouquet[3], G. Bayon[3], J.P. Foucher[3], J. Woodside[4], J. Mascle[5] and the Nautinil Scientific Party

[1] *UPMC, LOCEAN, Paris, France*

[2] *MNHN, Histoire de la terre, et CNRS, Paris, France*

[3] *IFREMER, Centre de Brest, Plouzané, France*

[4] *Free University, Amsterdam, The Netherlands*

[5] *Géosciences-Azur, Observatoire de Villefranche-sur-mer, France*

Abstract

During the Nautinil cruise (September-October 2003), mud volcanoes and pockmarks located in the central part of the Mediterranean Ridge (MR) (Olimpi area) and in selected areas of the Nile Deep-Sea Fan (NDSF), have been investigated at water depths ranging from 500 m to 3019 m. Authigenic carbonates, commonly associated to these fluid-venting areas, are composed mainly of aragonite and high-Mg calcite. Petrographic observations show that these carbonates are mostly constituted by microcrystalline carbonate cement in which bioclasts, detrital minerals and other authigenic phases (mostly pyrite, barite, gypsum) are included. The isotopic compositions of carbonates display very large variations ($-0.67 < \delta^{18}O$ ‰ V-PDB < 5.45; $-42.14 < \delta^{13}C$ ‰ V-PDB < 3.10). Most carbonates exhibit $\delta^{18}O$ values around 3‰ indicating that they have precipitated in isotopic equilibrium with bottom seawater. Higher $\delta^{18}O$ values are found in carbonates from the MR indicating the probable contribution of ^{18}O-rich fluids. Authigenic carbonates are typically depleted in ^{13}C, revealing that the major carbon source for those carbonates derives from methane.

1. Introduction

Mud volcanoes, pockmarks and seeps represent common superficial topographic features of cold seep environments, which particularly form along convergent plate boundaries on active continental margins and on passive continental shelves. They are created by ascent of water, mud and gas (mostly biogenic and/or thermogenic methane) originating from deeper sedimentary layers through the seafloor (Brown, 1990). In the Eastern Mediterranean, fluid-releasing structures were briskly discovered on the MR, closely associated with active, compressional and transcurrent tectonic lineaments (Camerghi *et al*., 1995; Woodside and Volgin, 1996; Kopf *et al*., 2000; Huguen, 2001; Dimitrov and Woodside, 2003), and, more recently, on the NDSF (Bellaiche *et al*., 1999, 2001; Mascle *et al*., 2000), closely controlled by over-pressure in sediments and/or salt-induced tectonics (Loncke and Mascle, 2004).

Carbonate precipitation is a striking phenomenon associated with fluid-releasing structures. It has been assigned as the result of the anaerobic oxidation of methane (AOM) (Ritger *et al.*, 1987; Paull *et al.*, 1992) mediated by a microbial consortium of archaea and sulfate-reducing bacteria (Boetius *et al.*, 2000; Michaelis *et al.*, 2002). This biogeochemical reaction produces a significant portion of bicarbonate ions, which increase carbonate alkalinity and precipitate as authigenic carbonate (Ritger *et al.*, 1987; Paull *et al.*, 1992; Aloisi *et al.*, 2000, Greinert *et al.*, 2001). These carbonates typically occur as crust pavements, slabs and mounds at the seafloor and the topmost sediments but also as concretions and micro-concretions dispersed in sediments. Previous investigations on the mineralogy and geochemistry of carbonate crusts from the Eastern Mediterranean showed that they are composed of a mixture of aragonite, magnesian calcite and dolomite, exhibiting negative $\delta^{13}C$ values, which clearly indicates that carbonate precipitation is closely related to AOM (Aloisi, 2000; Aloisi *et al.*, 2000).

This study presents the petrographic, mineralogical and geochemical data of carbonate crusts and concretions from different areas of the Eastern Mediterranean to decipher biogeochemical processes related to the formation of diagenetic carbonates and to identify the sources of carbon and water from which carbonates have precipitated.

2. MATERIAL AND METHODS

The carbonate crusts, concretions and sediments studied here were collected from the topmost sediments by the Nautile submersible during the Nautinil cruise (September-October 2003) on the Napoli mud volcano (1939 m water depth) located in the central MR (Olimpi area) and on selected mud volcanoes (MV), pockmarks and gas chimneys known on the distinct areas of the NDSF (Loncke and Mascle, 2004) (see Figure 1): 1) the Caldera area (2875-3032 m water depth) located in the Western part of the Nile margin domain, 2) the Pockmark area (1683-2132 m water depth) located in the Central part of the margin, 3) the Eastern area (991-1122 m water depth) and 4) on North Alex chimney (500 m water depth) located in the upper slope of the Central province.

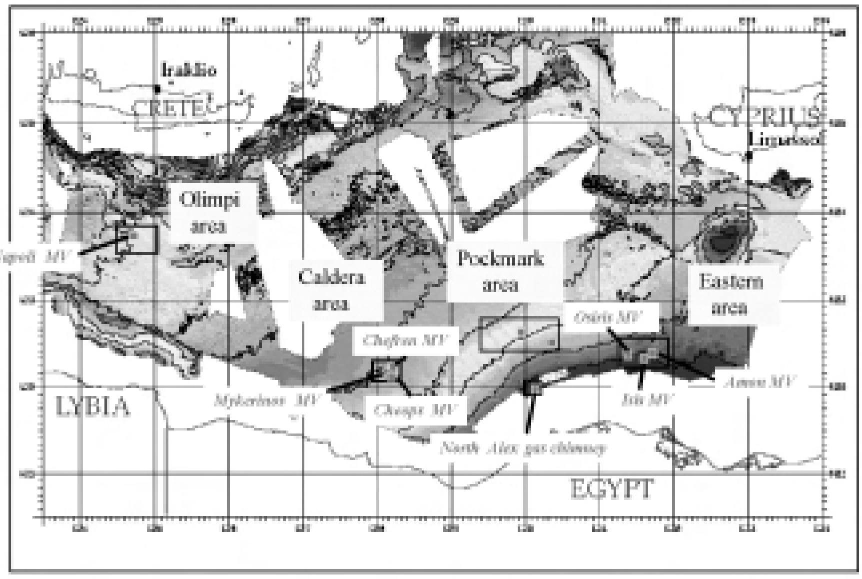

Fig. 1. Location map showing the dive areas where carbonate crusts and sediments were collected during the Nautinil cruise.

Carbonate content and mineralogical (XRD) analyses have been carried out on carbonate crust and concretion sub-samples. Semi-quantitative estimations (in weight %) of the different carbonate minerals were obtained using the peak areas in combination with total carbonate content. The petrography of selected carbonate crusts was studied in thin section using optical microscopy. The morphology, microstructure and elemental composition of selected crust fragments and millimeter-size concretions were examined with a scanning electron microscope (SEM) coupled with an elemental analysis unit. The oxygen and carbon isotope compositions of calcium carbonate, expressed in the conventional δ notation relative to Vienna PeeDee Belemnite (V-PDB) reference (Craig, 1957), were measured on powdered samples following the standard procedure of McCrea (1950).

3. Results and discussion

3.1. General characteristics of carbonate crusts and concretions

3.1.1. Mineralogy

Carbonate crusts and centimeter-size concretions are mainly composed of carbonates (from 63 to 96 wt% of the bulk sediment) associated with detrital minerals (clays, quartz, feldspars) and minor authigenic phases (mostly barite, gypsum and pyrite). Aragonite and calcite represent the dominant carbonate phases, associated with minor quantities of dolomite. Calcite often occurs as a mixture of low- and high-Mg calcite characterized by different *d* values of their (104) diffraction peak in X-ray patterns: the low-Mg calcite, most probably from calcite of pelagic sediments, mainly occurs between 3.035 and 3.030 Å, and, the high-Mg calcite, most probably constituted by authigenic calcite, is predominant between 3.000 and 2.995 Å. High-Mg calcite is always the most abundant calcite found in studied samples. Moreover, two groups of dolomite are also identified on the basis of the d(104) peak position: a Fe/Ca-rich dolomite group between 2.936 and 2.925 Å, and, a near stoichiometric dolomite between 2.900 and 2.882 Å.

3.1.2. Petrography

Most of the carbonate crusts form either centimeter-thick massive pavements and mounds or very porous pavements and slabs. Their upper surface is generally coated by a dark yellow to dark brown oxide layer and colonized by benthic organisms (worms, bivalves). Numerous sinuous tubular structures cross carbonate crusts and result from carbonate precipitation around worm tubes, which originally colonized the underlying unconsolidated sediment (Aloisi *et al*., 2000). Millimeter- to centimeter-size indurated burrows filled with fine-grained sediment and centimeter-length carbonate concretions corresponding to fossilized burrows or filled conduits are also found in sediment collected from the Pockmark and the North Alex areas, respectively. Thin-section and SEM observations of these crusts and concretions reveal that they are formed by a mixture of terrigenous (carbonate and silicate minerals) and biogenic (coccoliths, bolboforma, planktonic foraminifers, pteropods, bivalve shells, ostracods) components cemented by a microcrystalline carbonate matrix (Figure 2a). Large acicular aragonite crystals, under 20 μm in length, are generally present, associated with the compact micrite. These crystals have grown radially around bioclasts and filled voids, sometimes forming palissadic structures. Pyrite often occurs associated with authigenic carbonates, either as isolated grains (less than 10 μm in diameter), cubic crystals or framboids (14-15 μm in diameter), and provides evidence for bacterial sulfate reduction. Aggregates of authigenic copper sulfides crystals have also been observed in one carbonate crust from the Pockmark area. Few ovoid and elongated filament structures resembling bacterial colonies are observed in the upper surface of one carbonate crust from the Caldera area, suggesting the implication of microorganisms in carbonate precipitation. However, these structures could have been developed *in situ* or after sampling since samples were not stored under sterile conditions.

In unconsolidated sediments, millimeter-size carbonate concretions are abundant and result from a mixture of microcrystalline carbonates and pyrite cementing detrital minerals and clasts as shown by SEM observations (Figure 2c). Large acicular aragonite crystals can be observed at the surface of some micro-concretions and form palissadic structures (Figure 2b). Aragonite or high-Mg calcite is the predominant phase of these micro-concretions but ankerite, present as lens-shaped crystals sometimes gathered in rosette structure, also occurs in micro-concretions found in sediments from the Eastern area of the Nile Deep-Sea Fan (Figure 2c). Authigenic barite tabular crystals are often associated with authigenic carbonates, forming micro-concretions from the Pockmark area. Several pyrite concretions are also present in sediments derived from the pyritization of elongated tubes. Numerous millimeter- to centimeter-size twinned gypsum crystals with smoothed faces have been found in sediments from Isis and Amon mud volcanoes located in the Eastern part of the Nile Deep-Sea Fan and most probably precipitate from seeping sulfate-rich brines.

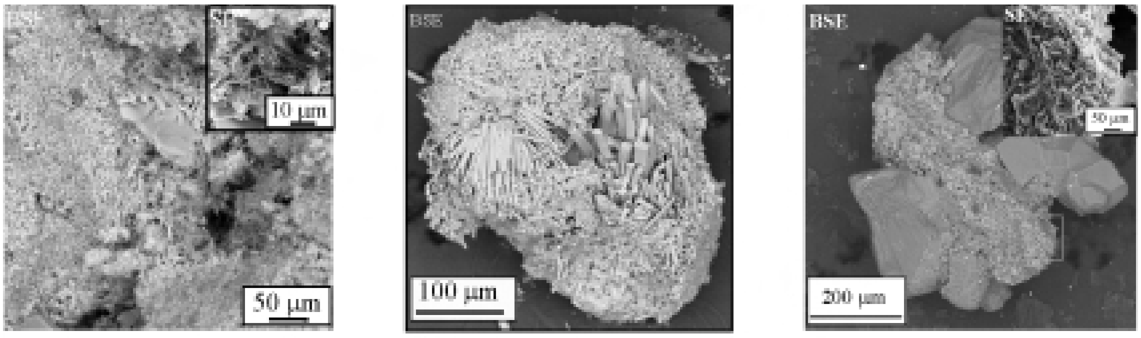

Fig. 2. SEM photographs of authigenic carbonate crust (**a**) and concretions (**b**, **c**) (BSE: back-scattered electrons, SE: secondary electrons). **a**: microcrystalline carbonate micrite (NL4CC1, Caldera area); **b**: large acicular aragonite crystals covering the surface of a carbonate micro-concretion (NL1PC3, Olimpi area); **c**: micrite composed by ankerite crystals cementing detrital clasts (NL9BC1 0-2 cm, Eastern area).

3.1.3. Stable isotopes

The oxygen and carbon isotopic compositions of diagenetic carbonate crusts and concretions exhibit a great variability as shown in Figure 3.

The $\delta^{18}O$ values of authigenic carbonates vary from 2.37 to 5.45‰ in the Olimpi area (MR) and from 2.36 to 4.15‰ in the different areas of the NDSF. As the oxygen isotope fractionation during the precipitation of aragonite and calcite is both controlled by the temperature and the $\delta^{18}O$ value of the surrounding seawater, the estimated $\delta^{18}O$ values of these carbonates precipitating in isotopic equilibrium with the modern eastern Mediterranean bottom seawater (T=13°C; $\delta^{18}O$=1.5‰ SMOW) would be 3.3‰ (Grossman and Ku, 1986) and 2.9‰ (Tarutani *et al.*, 1969), respectively. Thus, most of the studied carbonate crusts and concretions with $\delta^{18}O$ values around 3‰ were precipitated in isotopic equilibrium with the bottom seawater. High $\delta^{18}O$ values are generally observed in carbonate crusts and concretions from the Olimpi area

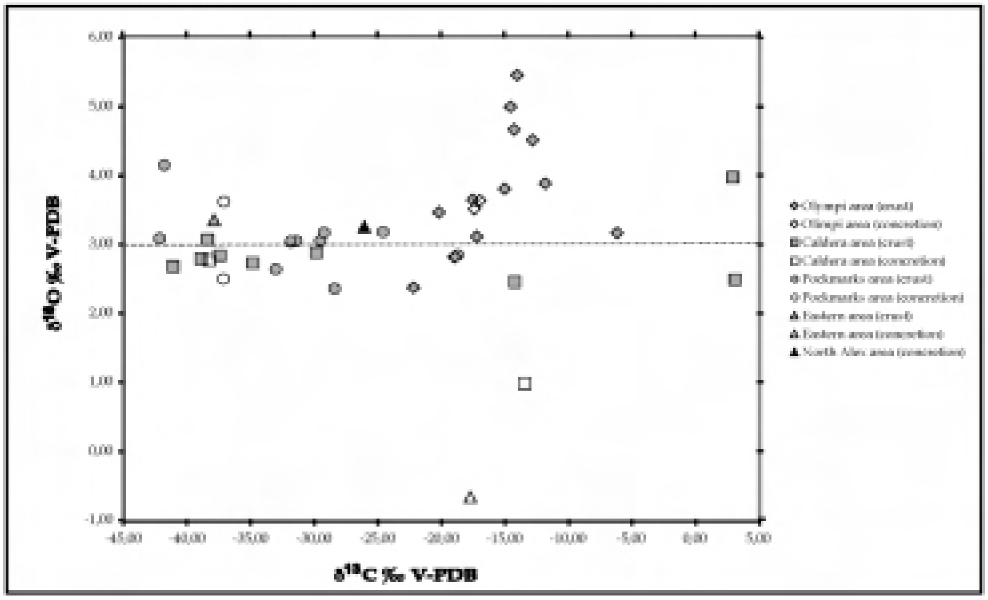

Fig. 3. Oxygen and carbon isotopic compositions of carbonate crusts and concretions from the MR and the NDSF.

(MR) indicating a contribution of ^{18}O-rich fluids, most probably brines and/or clay dehydratation. Two carbonate concretions from the Caldera and the Eastern areas exhibit low δ^{18}O values (0.98‰ and -0.67‰, respectively) showing either a local contribution from ^{18}O-poor water source (continental?) or, most probably, a local high heat flow. The relationship between isotopic fractionation of oxygen and temperature (Epstein *et al*., 1953), in carbonate-water system, indicates that calcium carbonate of concretion from the Caldera and the Eastern areas would have precipitated at 25.6°C and 18.2°C, respectively. These temperatures are consistent with the *in situ* temperature measurements in pore fluids which may reach more than 55°C above fluid-releasing structures (Foucher, unpublished data).

The carbon isotopic compositions of carbonate crusts and concretions from the MR and the NDSF span from -6.16 to -22.15‰, and, from -41.08 to 3.10‰, respectively. Similar δ^{13}C values of carbonate crusts, varying from -46.7 to 3‰, have been reported from the MR (Olimpi area) and the Anaximander Mountains in eastern Mediterranean by Aloisi (2000) and Aloisi *et al*. (2000). The carbon isotopic compositions of authigenic carbonates reflect the mixture of a marine source (pelagic sediments) with positive δ^{13}C values and a methane source oxidized by anaerobic bacteria with negative δ^{13}C values. Two carbonate crusts from the Caldera area exhibit positive δ^{13}C values, characteristic of carbonates precipitating in isotopic equilibrium with the modern eastern Mediterranean bottom seawater. Other carbonate crusts and concretions showing low δ^{13}C values are composed by a mixture of ^{13}C-depleted cement coming from the microbial anaerobic oxidation of methane and of sediments.

3.2. Vertical gradients

Mineralogical and geochemical analyses have been realized on sub-samples taken across a vertical section of a porous 6 cm-thick carbonate crust (NL7CC2) collected from the Pockmark area (Figure 4).

The vertical variations of the carbonate composition show that aragonite is the predominant carbonate in the upper six centimeters. High-Mg calcite and dolomite contents increase respectively from 0 to 7 wt% and from 0 to 5 wt% of carbonate content between the surface down to 6 centimeters depth. Mineralogical results obtained from high-resolution profiles across this crust performed by Bayon *et al*. (this volume) confirm these observations. As indicated by U/Th analyses (Bayon, this volume), this crust has grown downward resulting in the decrease in diffusing Mg^{2+} and SO_4^{2-} fluxes from seawater to the environment where carbonate precipitates. Thus, lower Mg^{2+} and SO_4^{2-} concentrations inhibit aragonite precipitation (Ritger *et al*., 1987) and favor the precipitation of high-Mg calcite and dolomite. However, the increase of high-Mg calcite content could also result from recrystallisation of aragonite.

The vertical variations of the δ^{18}O values in this crust show a downward increase from 2.82 to 3.37‰ as expected by the increase of dolomite content, a ^{18}O rich-carbonate due to different

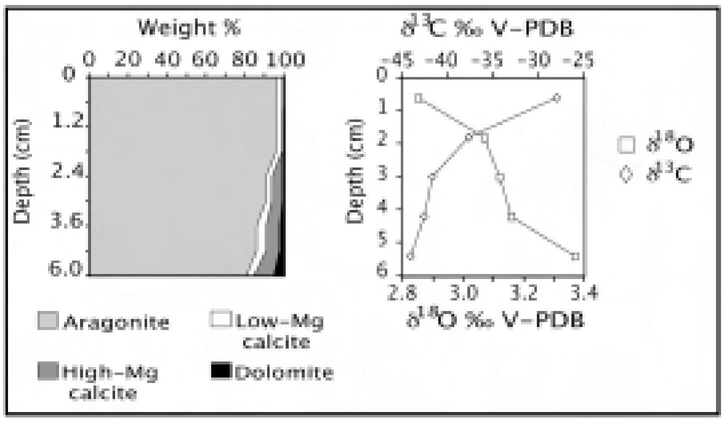

Fig. 4. Variations of carbonate mineralogy and stable isotopes compositions of $CaCO_3$ through NL7CC2 vertical transect.

oxygen isotopic fractionation during precipitation (Friedman and O'Neil, 1977; Land, 1985). Furthermore, the $\delta^{13}C$ values of calcium carbonates decrease regularly from -28.04 to -44.17‰ along the vertical profile indicating the increasing contribution of methane with depth.

4. CONCLUSION

Authigenic carbonate crusts and concretions are commonly associated with fluid-releasing features (mud volcanoes, pockmarks, gas chimney, etc.) of the MR and the NDSF. In all studied areas, authigenic carbonates are mainly formed by aragonite or high-Mg calcite associated with minor quantities of low-Mg calcite and dolomite. Carbonate concretions can be associated with other authigenic minerals such as barite, pyrite and gypsum. Isolated euhedral gypsum crystals precipitate from seeping sulfate-rich brines in sediments from Isis and Amon mud volcanoes (Eastern area). Most of the authigenic carbonates crusts and concretions are precipitated in isotopic equilibrium with the modern eastern Mediterranean bottom seawater. High $\delta^{18}O$ values are found in carbonates from the MR indicating that they have precipitated from a mixture of seawater and ^{18}O-rich fluids originated from great depths as evidenced by the pore water studies (Dählmann and de Lange, 2003; de Lange *et al.*, this volume). Two carbonate concretions from the Caldera and the Eastern (Amon mud volcano) areas are ^{18}O-depleted, more probably resulting from a higher heat flow at these sites. The low $\delta^{13}C$ values of authigenic carbonates indicate that the primary source of carbon was derived from the anaerobic oxidation of methane coming from the ascendant fluids.

Geochemical composition and origin for fluid and gas fluxes at Eastern Mediterranean mud volcanoes

Gert J. De Lange[1], V. Mastalerz[1], A. Dählmann[1], R. Haese[2], J. Mascle[3], J. Woodside[4], J.P. Foucher[5], V. Lykousis[6] and A. Michard[7]

[1] *Utrecht University, Faculty of Geosciences / Geochemistry, Utrecht, The Netherlands*
[2] *Geoscience Australia, Canberra, Australia*
[3] *Geosciences Azur, Villefranche-sur-mer, France*
[4] *Vrije Universiteit Amsterdam, FALW, Amsterdam, The Netherlands*
[5] *Ifremer, Brest, France*
[6] *HCMR, Athens, Greece*
[7] *CEREGE, Aix-en-Provence, France*

ABSTRACT

Expulsion of fluid and mud at eastern Mediterranean mud volcanoes seems mostly associated to enhanced fluxes of hydrocarbon gases, methane in particular. The salinity of the water phase in this mud ranges between brackish and hypersaline even within one mud volcano, whereas the solid phase may consist of fine clay boulders of several meters. In the seawater immediately above all mud volcanoes there is an enhanced methane content that may extend up to several hundred meters into the water column, with concentrations orders of magnitude higher than background values. The methane flux into the bottom water seems continuous but probably with varying intensity. On the basis of $\delta^{13}C$, δD, and the C1/C2+C3 ratio, the source of the gas is thermogenic, but with a potential diagenetic imprint. A relatively deep source with an anticipated formation temperature of 100 ^{o}C (+/- 20°C) is also suggested by empirical thermometers based on the pore water elemental composition of Na, K, and Mg in particular. Underlying Messinian ancient brines or evaporate horizons are the likely origin for the enhanced pore water salt content. At the most active sites of mud volcanoes, not only does the pore water concentrations of B and sometimes Li increase, but these are accompanied by a distinct shift in the $\delta^{13}C$ and δD of H_2O, going from typical seawater values at the uppermost sample to a distinctly deviating value (from +1.5 to +8 ‰, and from +8 to -25‰, respectively). These shifts are thought to be associated to clay mineral dehydration, i.e. the transfer of smectite into illite. This process is responsible for the greater part of the low salinities encountered at some mud volcanoes (Dählmann and De Lange, 2003). In the Anaximander area, Messinian evaporates are absent. Consequently, the fluids of the active mud expulsion sites in this area have low salinities, and these sites contain gas hydrates. The shallowest mud volcano where gas hydrates have been found (1,264 m) has a depth close to the edge of the gas hydrate stability field. In the Olimpi Field and Nile Fan mud volcano areas no gas hydrates have been recovered thus far. Although the methane content in the water column at all sites of this study indicates a continuous degassing, there are several observations

on mud expulsion that suggest that pulsed outflow is likely to occur at intervals of several 100 kyrs (Milano mud volcano), few kyrs (Kula mud volcano), and a few years (Napoli and Isis mud volcano). The major Menes caldera with its few sub-cones inside, and the concentric grabens around Amsterdam mud volcano may also be witness of such pulsed activity. In some places the continuous release of gas keeps the mud fluidized in an elongated vertical canal; these 'chimneys' can be sampled to great depths (tens to hundreds of meters) using traditional water column sampling tools.

INTRODUCTION

Eastern Mediterranean mud expulsion structures have been discovered and sampled from 1978 onward in various areas, but during the last decade in particular at Olimpi Field (OF), Anaximander Area (AA), and Nile Fan (NF). Most of these active fields seem grouped at the Mediterranean Ridge, where subduction of the African plate underneath the Eurasian plate is taking place or took place until very recently (Figure 1). The major exception, the Nile area, is unrelated to the Mediterranean Ridge and its associated deep processes. Clasts of mm to several cm have commonly been observed in sediments recovered from mud volcano (MV) structures in the eastern Mediterranean (Camerlenghi *et al*., 1992; several contributions in Cita *et al*., 1996).

The hypersaline pore waters associated to some of the active mud volcanoes have been attributed to the dissolution of underlying Messinian evaporates or to relict Messinian brines (Van Santvoort and De Lange, 1993; Vengosh *et al*., 1995). This continuous flux of dissolved salt into the deep Mediterranean is one of the factors that may contribute to the stabilization and potential stagnation of the deep Mediterranean water. The expulsion of high salinity fluid is not only observed at several MVs, most notably Napoli in OF where small brine lakes occur at its summit (MEDINAUT/MEDINETH, 2000), but also by brine lakes in areas that seem unassociated to MV fields (Tyro, Bannock, Urania, Atalante, and Discovery Basins) (De Lange and Ten Haven, 1983; Shipboard party Bannock, 1985; Medriff, 1995). Expulsion of water with reduced salinities have also been reported (De Lange and Brumsack, 1998; Dählmann and De Lange, 2003). In addition, enhanced methane concentrations have been observed at some active mud volcanoes in the eastern Mediterranean, with concentrations well above background values (Charlou *et al*., 2003; this study). This contribution will focus on composition and origin of gas and fluid expulsion

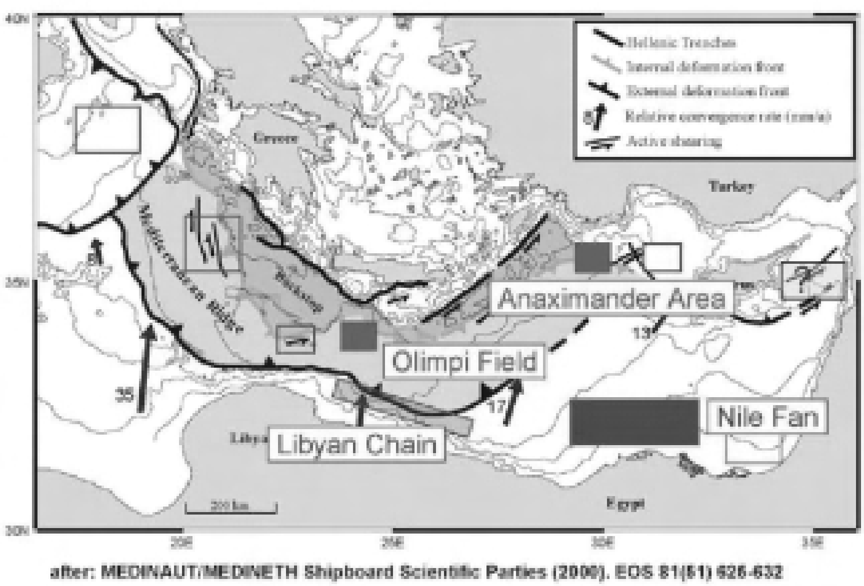

Fig. 1. Eastern Mediterranean mud volcano areas and Mediterranean Ridge; filled squares are areas discussed in this contribution.

observed during recent cruises to mud volcano areas at the active (OF, AA), and passive (NF) margin of the eastern Mediterranean

RESULTS AND DISCUSSION

In recent years, integrated studies of fluid systems in the eastern Mediterranean were dedicated to the Olimpi Field and in particular to Anaximander Area and Nile Fan. These studies were done using RV *Nadir* (1998), RV *Logachev* (1999), RV *Pelagia* (2000,2001), RV *Atalante* (Sept. 2003), RV *Aegeo* (May 2003, Nov.2004), and RV *Pelagia* (May 2004), and will be continued in 2006 using RV *Meteor*.

Initially, clasts of mm to several cm and of ages down to Pliocene or even Cretaceous have been found in sediments recovered from mud volcano structures in the eastern Mediterranean (Camerlenghi *et al*., 1992; Cita *et al*., 1996 and several papers therein). During ODP Leg 160 and subsequent observations during submersible dives, have demonstrated that boulders of several meters occur at MV structures (Emeis *et al*., 1996; Robertson *et al*., 1996b). In addition, ODP observations have indicated that pulsed MV mud expulsion activity must have taken place at variable frequencies. Napoli MV seemed recently active and relatively young, whereas the activity at Milano MV appeared much older and at intervals in the order of 100 kyrs. The continuous activity at Napoli MV is much more apparent than that at Milano MV, in that during a more than 15 year period brine and gas-rich sediments have been recovered from its summit. Nonetheless shifts or different phases in activity seem to occur, which is not only clear from different pore water compositions, but also from brine lakes that appear and disappear (NAUTINIL, 2003). Similar, recent, pulsed activity during the last few years is evident for Isis MV (see also Feseker *et al*., this volume), whereas larger intervals of episodic eruptions are clear forMercator MV in the Cadiz area (see Henriet *et al*., this volume). Episodes of enhanced mudflow are also apparent at Kula MV in AA, where distinct flows at its summit have been found to occur in episodes of a few kyrs (ANAXIMANDER project). In summary, and similar to lava volcanoes, a range of periodicities in MV activity appears to occur, from continuously active (compare Stromboli lava volcano and Napoli/Isis mud volcanoes) to episodically (compare Vesuvius lava volcano and Milano/Mercator mud volcanoes).

Different phases of activity could also be deduced from the concentric grabens around / at Amsterdam MV and the occurrence of a small active side cone MEDINAUT and MEDINETH projects). This could either indicate a major initial activity phase, followed by a possibly pulsed decreasing activity and consequent collapse structures. A similar observation can be made for the major Menes caldera, itself having a diameter of 8 km (Huguen *et al*., this volume), and small subsidiary cones now inside, suggesting a major initial phase followed by continued activity but at much smaller dimensions. Two out of the three sub-cones within Menes caldera are actively releasing gas, brine fluid, and mud, whereas a third one is 'empty' and seems inactive at present. It seems therefore that major MV activity is largely episodic, whereas relatively small scale 'pressure-release' may be relatively continuous but not necessarily remaining at the same exact outcropping locality. It is only at these relatively small scale fluid expulsion sites with relatively small expulsion rates, that samples could be taken for studies of gas and fluid composition. As a consequence, 'en-route' processes are likely to alter the initial composition progressively and to an extent that is inversely proportional to the expulsion rate. In the following, we will first discuss the gas, then the fluid expulsion characteristics, and finally gas/fluidized-mud chimneys.

Gas expulsion and gas hydrate occurrence

Expulsion of fluid at eastern Mediterranean MVs seems mostly associated to enhanced fluxes of methane. This is noticeable by the methane concentration in the deep water at MVs that is orders of magnitude higher than in deepwater unassociated to MVs. These enrichments may expand from the MV summit to several hundred meters up into the water column. They are usually associated with enhanced light scatter, which can be attributed to either suspended matter or small gas bubbles as has been shown for the Black Sea by Naudts *et al*. (in press). As we did not observe increased suspended matter in samples taken at Amsterdam MV, we conclude that it is methane bubbles rather than suspended matter that characterizes the observed enhanced light scatter in our water column profiles. These profiles show a close association of light scatter, enhanced methane and reduced oxygen contents. Near-bottom methane content increased going from Olimpi Field (Napoli MV), to Anaximander Area (Kula, Kazan, Amsterdam MVs) to Nile Fan (Menes caldera, North Alex, Isis MVs) (Figure 2).

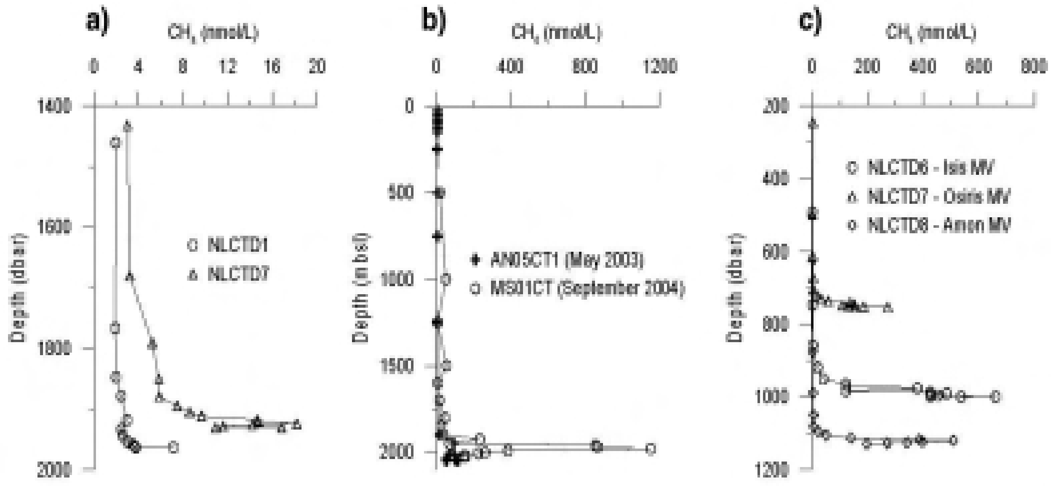

Fig. 2. Water column methane contents for **a**) Napoli MV at Olympi Field; **b**) Amsterdam MV at Anaximander Area; **c**) Nile Fan. Note different concentration scales.

Our repeated sampling at Amsterdam MV has demonstrated the continuous activity of methane release into the water column between 1999, 2003, and 2004. Most of the sediment recovered at Amsterdam and Kazan MV contained gas hydrate (GH), usually being finely dispersed but occasionally as a lump. Most MVs in the Anaximander area contain GH, even at a water depth as shallow as 1,265 m, which is close to the boundary of the gas hydrate stability field. So far no GH has been observed in sediments of the Nile Fan. The reasons therefore are twofold: a) Most of the sites sampled lie in water depths well above the GH stability (Figure 2), and b) At Menes caldera sub-cones Chefren and Cheops, it is the enhanced temperature within the fluidized mud chimneys that prevents GH to form. Potentially at the edges of these latter sites, favourable conditions for GH formation may occur.

The hydrocarbon gas composition, together with their isotopic signature, points to a geothermal rather than biogenic gas origin for all sites studied thus far (Figure 3). As stated above, the composition may have been altered due to ongoing diagenetic processes. The composition considered to be most ‘initial’ is that of the deepest sediments at sites of highest advection rates. If such ‘initial’ composition is compared with the composition of hydrocarbons found in the water column, it appears that these are rather similar. This observation supports our previous statement of bubble entrainment into the water column, and points to a direct injection rather than a diffusive transport of gas into the water column. At the MVs reported here, a few observations of bubble release have been made, in particular but not only during bottom sampling with the submersible Nautile, but no sites of continuous gas bubble release have been detected. However, at Amon MV, acoustic ‘clouds’ have been observed during a bottom-tow survey (Dupré *et al.*, this volume). A semi-diurnal release, as observed in other regions more prone to tidal pressure differences, is not expected here. Nonetheless, an episodic rather than a continuous release of gas bubbles seems the most likely mechanism for bringing gas into the water column at eastern Mediterranean MVs.

It seems therefore that in the Anaximander area and even more so in the Nile Fan area, major expulsions of gas occur into the water column.

The measured methane concentrations in the sediments are similarly high for both areas, ranging from 1 to 3 mmol/L for the Anaximander area and from 1.5 to 3.5 mmol/L for the Nile area. In contrast, the salinity of the advecting fluids originating from underlying sediments is dramatically different between the two areas. This is related to absence and presence of the Messinian evaporate interval. Clearly, it is not the Messinian evaporite horizon that makes the difference for the occurrence of large methane fluxes. This suggests that capping of the gas by an evaporate horizon is not a prerequisite for gas accumulation in the eastern Mediterranean.

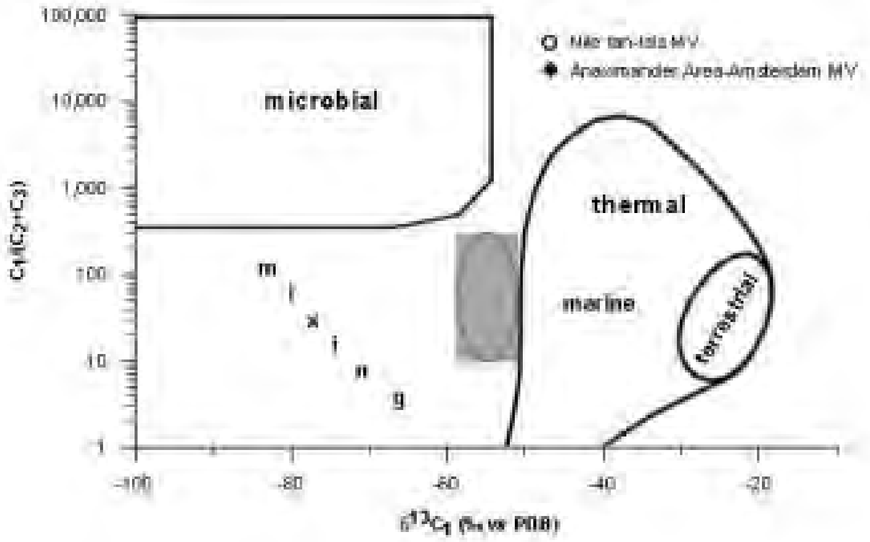

Fig. 3. C1/C2+C3 vs d13C.CH4 diagram demonstrating the commonly assumed relationship between composition and potential fields of origin for methane (after Luckge *et al.*, 2002).

Fluid composition and origin

The active top part of the Anaximander mud volcanoes is usually characterized by fluids of reduced salinities, whereas those in the Nile area have near-normal salinity to brine composition, and those in Olimpi Field have reduced salinity to brine composition. Since the most extreme differences observed thus far occur in the Olimpi area, we will illustrate the various processes that may be involved using these sites in particular. During ODP Leg 160, four holes at each of the two MV (Napoli and Milano) were drilled. Additional Boxcore, Gravity core, and Giant pistoncore sampling took place prior to and post ODP sampling. The ODP data set will be used mainly, providing the deepest samples. There is a clear difference between the crestal and flank sites for each MV. At Napoli MV the crestal sites have a chlorinity at all depths that is much higher than that in the bottom water (5400 vs 600 mM Cl) whereas at the flanks the chlorinity increases from a normal seawater value close to the sediment/water interface to enhanced levels deeper down in the sediment. A similar picture is seen for the flank sites at Milano MV, but the crestal sites are completely different, having a salinity that is well below that of ambient seawater (60 versus 600 mM Cl) (Figure 4). Despite the extreme difference in crestal salinity, the stable isotope data for H_2O at both sites are rather similar (Figures 5, 6) with d18O increasing and d2H decreasing with depth in the sediment.

The enhanced salinity at Napoli MV has been attributed to underlying Messinian evaporates (e.g. Van Santvoort and De Lange, 1995). The reduced salinity at Milano MV had initially been attributed to the decomposition of gas hydrates upon recovery of the sediment (De Lange and Brumsack, 1998) which has later been rectified on the basis of stable isotopes (Dählmann and De Lange, 2003). The various pathways that lead to a shift in the fluid stable isotope composition are displayed in Figure 6; clearly our data are in the field of clay mineral dehydration (cf. Dählmann and De Lange, 2003). In addition, other pore water constituents are in line with this observation, namely the distinct decrease in K in all crestal sites (Figure 7). An intense interaction at elevated

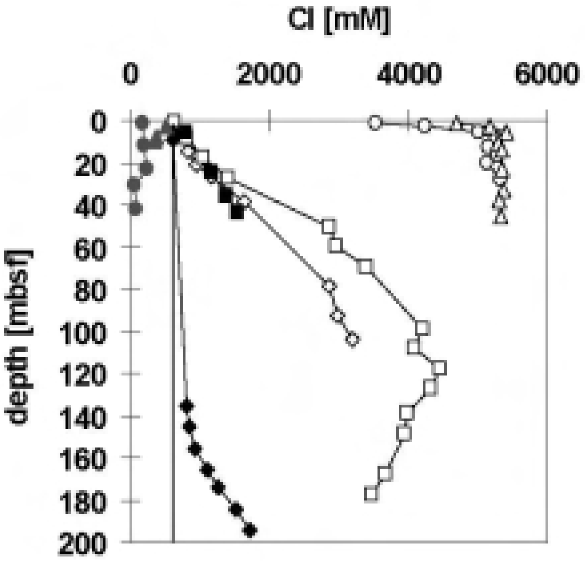

Fig. 4. Chloride pore water concentration at Napoli MV ODP-site 971 (open symbols) and Milano MV ODP-site 970 (closed symbols). Crestal sites (open and closed triangles and circles) are more shallow due to drilling safety precautions because of high methane contents than flank sites (open and closed squates and diamonds).

temperatures is suggested by the enhanced pore water concentrations of B (and at some sites Li). In addition, applying the empirical geothermometer equation of Giggenbach (1988) based on the pore water elemental composition of Na, K, and Mg in particular, results in a formation temperature of around 100 ^{o}C (cf. Haese *et al*., 2003, 2005). Such enhanced interaction of liquid and solid phase potentially at greater depth, is also indicated by pore water $^{87}Sr/^{86}Sr$ values of 0.70810. Such a value, clearly different from that of present-day Mediterranean seawater (0.709165; De Lange *et al*., 1990b) suggests intense interaction with potentially volcanic material. Alternatively, part of the difference can also be attributed to an upper Miocene age of the Sr. An average value for Mediterranean Messinian seawater $^{87}Sr/^{86}Sr$ of 0.70898 has been reported (De Lange *et al*., 1990a, b) whereas Paytan *et al*. (1993) reported a value for upper Miocene seawater of 0.70891. A leached (Chester-Hughes) sediment sample from Napoli MV

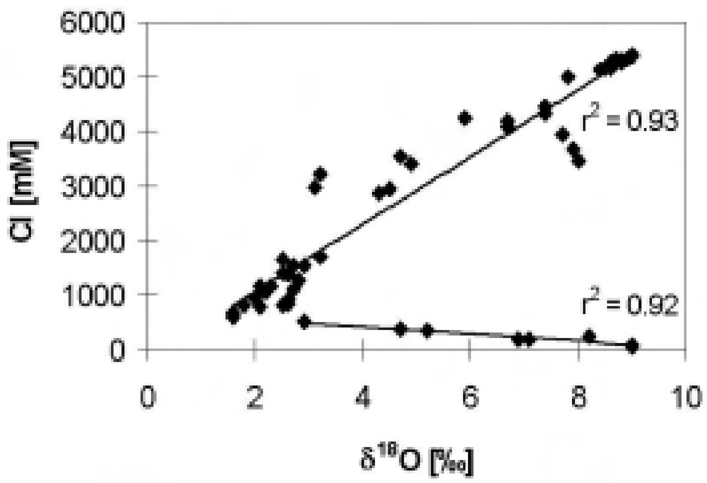

Fig. 5. d18.O of H_2O increases irrespective of salinity, as indicated by chloride content of pore fluid.

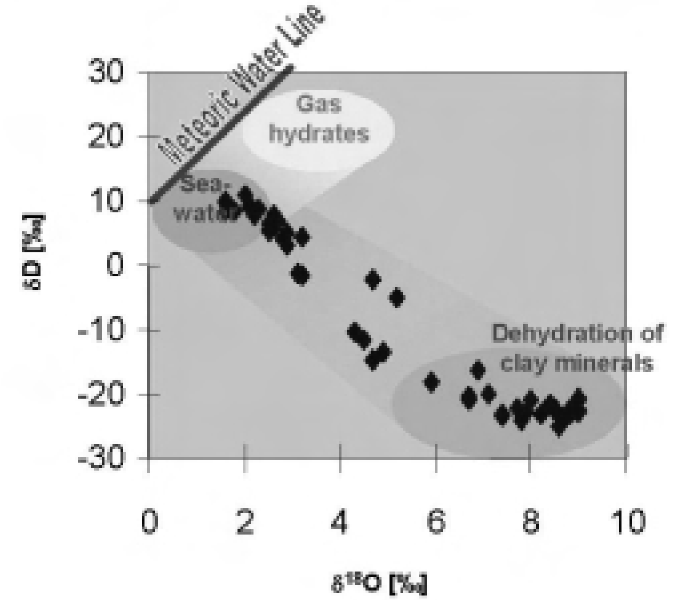

Fig. 6. Processes causing C1 freshening with their respective impact on d18O / d2H of the fluid; samples of IDP 160 sites 970 and 971 at Napoli and Milano Domes are indicated in diamonds (after Daehlman and De Lange, 2003).

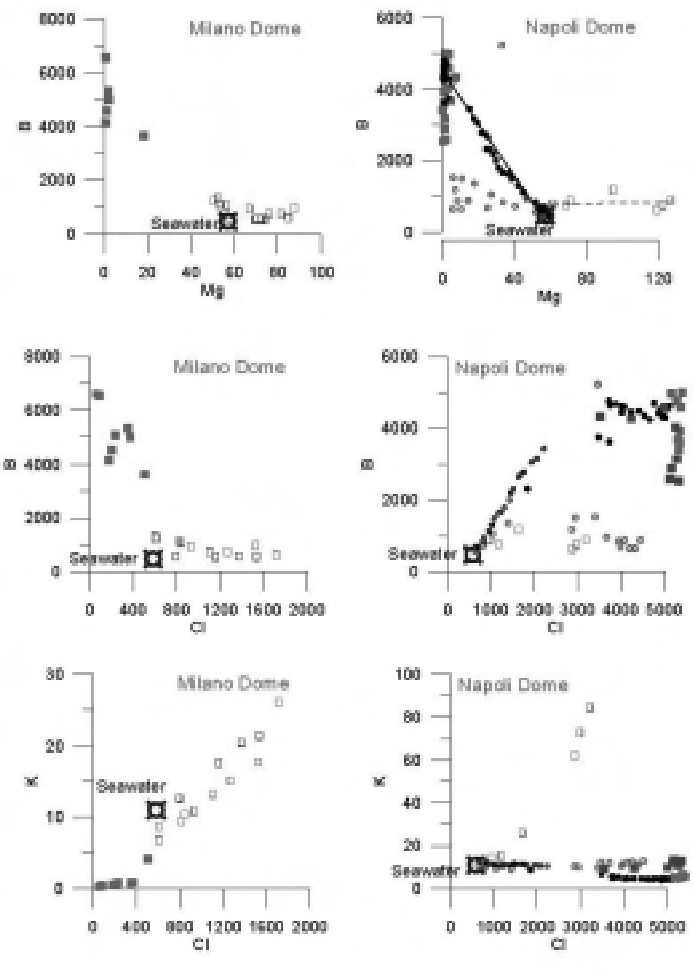

Fig. 7. Pore water Mg, B, K and Cl for Milano (left panels) Napoli (right panels) MV, collected during cruises from 1991 onward.

resulted in distinctly different $^{87}Sr/^{86}Sr$ signatures for leachate and residue (0.70834 and 0.710987, respectively). The leachate E_{Nd} results (-2.7 and -5.9 respectively) are in accordance with this observation and with the pore water result discussed above. However, if the leachate $^{87}Sr/^{86}Sr$ signature is to be fully attributed to ancient carbonate, then a minimum age of 22 Ma can be deduced.

In summary, irrespective of salinity, a deep source, enhanced temperature and fluid/rock interaction seems common for fluid and for gas expulsed at eastern Mediterranean mud volcanoes.

Gas-fluidized-sediment chimneys

In the Nile Fan, enhanced salinity is encountered only at a few locations, in particular at Cheops and Chefren MVs situated inside the large Menes caldera. These two sub-cones are peculiar sites also for the occurrence of fluidized mudpits. They have enhanced salinities and temperatures, being 150 ‰ and 57°C at Chefren and > 300 ‰ and 37 / 25°C at Cheops MV. Using three adapted-CTD casts inside these muddy brine structures, the liquid mud was sampled for gas, and water-phase geochemical analyses. Furthermore, we took a piston and gravity core. At both sites, the obtained profiles are rather constant with depth and do not differ between cores and accompanying brine-CTDs.

The depth of the mud-brine is approximately 300 meters at Chefren MV and 10 meters at Cheops MV, which needs to be compared to a <80 m depth of the Menes Caldera itself. The Si concentration in the cores is reflecting these temperatures with higher values at Chefren MV (500-600 μM) and lower values at Cheops MV (300 μM). Hydrogensulfide was found in higher concentrations in the central cores of Chefren MV (up to 1.5 mM), and only in minor amount at Cheops MV. The Chefren sub-cone within the Menes caldera is a special case in that it resembles a rusted kettle, leaking, possibly Fe-rich, brines near its bottom, and boiling at its top. It seems that a continuous release of gas, in particular methane, is fluidizing the sediment until considerable depth. In fact the sediment within this chimney remains fluid till at least 200 m below the 'surface' of the Chefren summit, i.e. to more than 150 m below the Menes caldera bottom.

Such chimneys offer a 'window' to fluid and gas that have a more initial composition than that encountered at the sediment surface. The actual sampling of such structures is a real challenge, not only technically but also analytically. This gas venting has not resulted in clear, distinct gas venting sites at the surface, but rather in irregular bubble release at different and probably variable sites within the Chefren summit area.

Acknowledgements

We acknowledge the support given by captains and crews of the research vessels that were all dedicated to give us the best possible samples. The assistance given by cruise participants, and in particular the analytical assistance by H. de Waard, G. Nobbe, R. Knoop, S. Gusic, A. van Dijk, R. Baarends (all at UU), E. Weerlee, K. Bakker, J. van Ooijen (all NIOZ), is gratefully acknowledged.

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Temporal activity of fluid seepage on the Nile Deep-Sea Fan inferred from U-Th dating of authigenic carbonates

G. Bayon[1], G.M. Henderson[2], C. Pierre[3], M. Bohn[4] and Y. Fouquet[1]

[1] *Département Géosciences Marines, Ifremer, Plouzané, France*
[2] *Department of Earth Sciences, Oxford University, Oxford, UK*
[3] *LOCEAN, Université Pierre et Marie Curie, Paris, France*
[4] *Microsonde Ouest, CNRS-UMR 6538, Ifremer, Plouzané, France*

ABSTRACT

Oxidation of methane-rich fluids in cold seep environments typically leads to the precipitation of authigenic carbonates. Here we report ^{230}Th/U ages for carbonate crusts recovered from cold seeps on the Nile Deep-Sea Fan. Our aim has been to investigate whether U-Th dating methods could be applied successfully on cold seep carbonate-cemented mudstones. This study is directly relevant to the current effort at better understanding the dynamics of fluid venting systems on continental margins (e.g. pockmarks, mud volcanoes) during the Late Quaternary. We show that U-Th dating of such carbonate-cemented mudstones is challenged by detrital contamination significantly. However, whenever carbonate precipitation processes have allowed the precipitation of well-crystallised aragonite (e.g. fibrous aragonite in porous crusts), careful sampling of those aragonite-rich areas by micromilling techniques allows successful ^{230}Th/U dating using isochron methods. Measured ^{230}Th/U ages on cold seep carbonates can provide unique information on temporal activity of fluid seepage on the Nile Deep-Sea Fan over the last thousands of years.

1. INTRODUCTION

Submarine pockmarks are widespread features on continental margins, which are often related to cold seeping of gas-rich fluids on the seafloor and/or presence of gas hydrates in marine sediments. Over recent years, there has been much interest in the study of submarine pockmarks because they represent potential pathways for important quantities of gas from sediments to the ocean. In active pockmarks, the expulsion of gas-rich fluids supports the development of chemosynthetic communities and the formation of authigenic carbonates, both of which are of interest for the understanding of geomicrobiological and biogeochemical processes related to cold-seep environments. One outstanding but yet unresolved issue in cold seep-related studies is to determine when submarine pockmarks have formed and how fluid activity has evolved through time, over the last few thousand years. This is of special significance for understanding which global processes (e.g. tectonic constraints, mass-wasting processes, gas hydrate destabilisation, climate change) are responsible for triggering circulation of gas-rich fluids to the seafloor.

Evidence for past fluid flow and episodes of gas hydrate destabilisation in marine sediments has come primarily from carbon isotope signals in geological records (Dickens *et al*., 1995; Krull and Retallack, 2000; Hesselbo *et al*., 2000; Kennett *et al*., 2000; Hill *et al*., 2004). Because methane in cold seep environments exhibits typically highly negative carbon isotope signatures ($\delta^{13}C$ ~ -65 per mil), large negative $\delta^{13}C$ excursions recorded by foraminifera in marine sediments have been interpreted as indicators of intense fluid flow and/or dissociation of methane hydrates (Wefer *et al*., 1994; Kennett *et al*., 2000; Smith *et al*., 2001; Keigwin, 2002; Rathburn *et al*., 2003; Hill *et al*., 2003, 2004). It is still unclear, however, whether the $\delta^{13}C$ signature of seep foraminifera does truly reflect that of surrounding pore waters from which they have precipitated or whether it may be acquired later, after deposition, during diagenetic processes (Torres *et al*., 2003; Cannariato and Stott, 2004; Martin *et al*., 2004).

Authigenic carbonates represent potential archives of past fluid flow and gas hydrate formation and dissociation on continental margins (e.g., Sample and Kopf, 1995; Bohrmann *et al*., 1998; Naehr *et al*., 2000; Greinert *et al*., 2001). They result primarily from the microbial anaerobic oxidation of methane (AOM) in sediments (e.g. Boetius *et al*., 2000). The occurrence of authigenic carbonate deposits (e.g. chemoherm carbonates, carbonate crusts and nodules) has been reported widely at many cold seep locations. Absolute dating of cold seep carbonates would provide an excellent means for reconstructing past fluid flow and the evolution of any gas hydrate reservoir in marine sediments through time. Unfortunately, conventional ^{14}C dating technique is not applicable to cold seep carbonates because their carbon derives partly from old fossil sources (i.e. methane). Recently, Teichert *et al*. (2003) have demonstrated that U/Th dating techniques could be applied successfully to cold seep carbonates. In their study, they have reported $^{230}Th/U$ ages for a series of chemoherm carbonates and pure aragonite concretions collected on the seafloor by video-guided grab sampler, at the Hydrate Ridge (Cascadian margin).

Here, we report U/Th analyses for various carbonate concretions collected from pockmarks off the Nile margin. Authigenic carbonates used for this study were collected by the Nautile submersible during an expedition on the Nile Deep Sea Fan (Nautinil, Mediflux ESF Program), in 2003. Our approach has been different to that of Teichert *et al*. (2003). We have attempted to date lithified carbonate crusts rather than pure aragonite concretions from the near-seafloor environment. Although such study may offer an unique opportunity to investigate the temporal activity of pockmarks on the Nile Deep-Sea Fan during the Late Quaternary, it may be complicated, however, by diagenetic issues (Luff *et al*., 2005) and the presence of significant initial ^{230}Th derived from terrigenous material.

2. Material, geological setting and methods

Material and geological setting:

Four carbonate crusts (NL6-cc1; NL7-cc1; NL7-cc2; NL14-cc5) and 3 sediments analysed in this study were recovered from the Central Province of the Nile Deep Sea Fan. The Central Province is an area of intense sediment destabilisation, between 1700 m and 2500 m water depth, characterised by a rough and chaotic morphology (Loncke *et al*., 2002a). The whole area corresponds, most probably, to a series of debris-flow deposits. Surface sediments also show repeated undulations and normal faults, which can be attributed to downslope gliding. Acoustic images reveal the presence of numerous highly-reflective patches (dark spots), which have been attributed to fluid-seeping structures (e.g. pockmarks, carbonate deposits, Loncke *et al*., 2004). During the Nautinil cruise, *in situ* observations from the submersible have confirmed that those acoustic patches do correspond to carbonate build-ups linked to fluid seepage. In this area, fluid escape on the seabed is probably induced by dewatering, most likely in response to sediment loading. Therefore, dating of authigenic carbonates collected from this Central Province is important for providing additional constraints on the relationship between slope instabilities and fluid circulation in this area.

In addition, two other carbonate crusts recovered from the upper slope of the Central Province (NL15-cc1) and the Eastern Province (NL11-cc2) have been analysed. Those two crusts were collected in close proximity to mud chimneys: the Amon Volcano (~1150 m water depth) and North Alex (~500 m water depth), respectively.

Petrography and mineralogy of authigenic carbonates:

All authigenic carbonate samples studied here correspond to carbonate-cemented mudstones. NL6-cc1, NL14-cc5 and NL11-cc2 are lithified carbonate crusts cemented by a homogeneous fine-grained aragonite-rich matrix. NL15-cc1 carbonates correspond to small centimeter-size aragonite rich concretions with irregular shapes. Those concretions are composed of homogeneous fine-grained aragonite-rich cement. Carbonate sample NL7-cc1 corresponds to a burrow filled by homogeneous and lithified high-Mg fine-grained carbonate cement. NL7-cc2 is a highly porous 6 cm-thick crust, exhibiting gradual mineralogical changes from top (aragonite dominant) to bottom (high-Mg carbonates dominant), which suggest that it has formed under changing diagenetic conditions. In this crust, fibrous crystals of aragonite (up to 800 μm length) have developed typically in open pore spaces, either in cracks or inside the cavities of biogenic components (e.g. foraminifers, bivalve shells).

Analytical methods:

Selected areas of carbonate concretions were hand-drilled carefully to obtain between ca. 50-100 mg of carbonate powder. However, mudstone carbonates may be highly heterogeneous and such 'large' samples are also likely to be contaminated by detrital material, which may affect U-Th dating significantly. Therefore, to try to reduce any possible contamination from detrital phases, some carbonate samples were also collected using a computer-assisted microsampling device (MicroMill). This system enables the sampling of micrometer-size areas of polished sections. For those carbonate samples, sampling areas were selected first using scanning electron microscopy. About ~ 1 mg of carbonate powders was collected for each sample for U-Th analysis. For sediments, about 50 mg of dried sediment were crushed into powder in an agate mortar. U-Th separation and analytical procedures have been inspired from the work of Robinson *et al.* (2002). U and Th have been analysed on a series of carbonates and sediments from the Central Province by MC-ICPMS (Nu Plasma Instrument, University of Oxford).

3. ^{230}TH/U DATING APPROACH

Measured carbonate (^{230}Th/^{232}Th) ratios are generally low (<12), due to both the young age of carbonates (low ^{230}Th ingrowth) and detrital contamination (high initial ^{230}Th). For lithified carbonates, (^{230}Th/^{232}Th) ratios of carefully selected micromilled samples (<1 mg) are as low (<3) as those corresponding to bulk carbonate samples (~ 100 mg). This shows that it is very difficult to sample a detrital-free authigenic phase (i.e. suitable for ^{230}Th/U dating) from those fine-grained and homogeneous samples. By contrast, micromilled samples for the porous crust NL7-cc2 exhibit much higher (^{230}Th/^{232}Th) ratios than corresponding bulk carbonates. This indicates that micromilling here has been successful for separating carbonate (aragonite) phases from detrital-rich areas within the crust. However, for all studied carbonate samples, detrital contamination is too high for allowing the calculation of ages using the conventional ^{230}Th age equation, which assumes initial ^{230}Th/^{238}U = 0, and requires instead the use of isochron methods (e.g. Bourdon *et al.*, 2003).

Isochron dating method considers each sample to be composed of a mixture of two components (e.g. detrital material and pure carbonate). By analysing several subsamples of similar age but with different proportions of the two components, it is possible to calculate the age corresponding to the detrital-free end-member (e.g., Edwards *et al.*, 2003). In this study, we have defined a sediment end-member, assumed to be representative of the detrital fraction incorporated by carbonate breccias. This sediment end-member has been defined as the average of three sediments from the Central Province of the Nile Deep Sea Fan. For lithified carbonate samples, as a consequence of an important ^{230}Th detrital contamination, only two meaningful ages have been obtained (for NL14-cc5_base and NL11-cc2 samples), with large associated errors (± ~ 3 kyr). Calculated isochron ages for NL7-cc2 samples are most satisfactory than those for lithified carbonate samples, ranging from ~ 9.5 to ~ 1.0 kyr BP with errors generally smaller than ± 1 kyr.

4. Discussion and implication for the link between slope instabilities and fluid seepage on the Nile margin

Our age profile for crust NL7-cc2 is shown in Figure 1. Calculated ^{230}Th/U ages vary from the upper part (~9.5 kyr BP) to the bottom-part of the crust (~1 kyr BP). This indicates that the crust is growing downward. Average growth rate for NL7-cc2 carbonate crust is ~ 500 yr/cm. Mineralogical and high-resolution geochemical profiles across a perpendicular section of crust NL7-cc2 have revealed that aragonite is abundant in the upper part of the crust whereas the proportion of high Mg-calcite increases toward the bottom part (Figure 1). This suggests that the formation of Mg-rich carbonates is favored over aragonite as the crust grows downward. This reflects most likely a gradual change towards sulfate-poor pore waters when the crust becomes progressively isolated from seawater.

In the Central Province of the Nile Deep-Sea Fan, the pathways for gas-rich fluids ascending to the seafloor is likely controlled by the internal structure of the destabilized sedimentary cover. Our calculated U-Th ages for authigenic carbonates from the Central Province suggest that fluid-venting in this area has been active since the early Holocene (~8-10 kyr BP). This period coincides with an intensified African moonson, during which the Nile river discharge is known to have significantly increased. In this context, one hypothesis would be that enhanced riverine discharge during the early Holocene has favored slope instabilities on the Nile fan, leading to significant overpressures within sediments from the central province and, ultimately, to fluid-seeping activity and formation of authigenic carbonates.

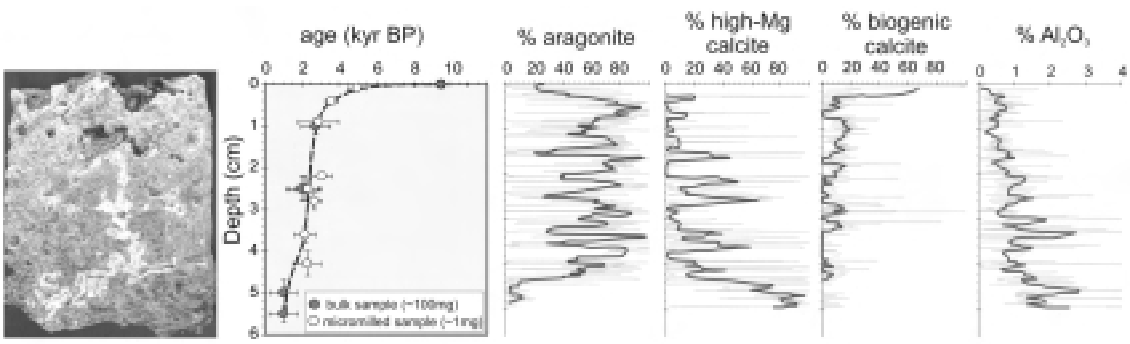

Figure 1. ^{230}Th/U ages and mineralogical high-resolution profiles across NL7-cc2 crust.
Relative proportions (wt. %) of aragonite, high-Mg carbonates and biogenic calcite have been calculated using a 4 end-member mixing model, based on Sr/Ca and Mg/Ca ratios measured by electron microprobe (Microsonde Ouest, Ifremer) on a polished section of NL7-CC2 crust cut perpendicular to its growth banding.

5. Conclusions

Overall, our U-Th data indicate clearly that contamination by detrital material places a strong limitation on our ability to date carbonate-cemented mudstones. The large uncertainties associated with calculated ages for lithified carbonates are due to the small dispersion of both (^{230}Th/^{232}Th) and (^{238}U/^{232}Th) ratios between carbonate samples and the sediment end-member. However, whenever carbonate precipitation processes have allowed the precipitation of well-crystallised aragonite (e.g. fibrous aragonite in porous crusts), careful sampling of those aragonite-rich areas by micromilling techniques allows successful ^{230}Th/U dating using isochron methods. Measured ^{230}Th/U ages on cold seep carbonates provide unique information on temporal activity of fluid seepage on the Nile Deep-Sea Fan through the last thousands of years.

Thermal and geochemical evidence for episodic mud eruptions at a mud volcano? The Isis mud volcano case.

Tomas Feseker[1,2], Anke Dählmann[3] and Jean-Paul Foucher[2]

[1] *Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany*
[2] *Ifremer, Brest, France*
[3] *University of Utrecht, The Netherlands*

INTRODUCTION

The Nile Deep-Sea Fan is the most important sedimentary accumulation in the eastern Mediterranean. Two geophysical mapping campaigns conducted in 1998 (Prismed II) and 2000 (Fanil) resulted in a first detailed morphostructural description of this deep-sea fan (Mascle *et al.*, 2001; Loncke *et al.*, 2002b; Loncke *et al.*, 2004) and led to the discovery of several circular and sub-circular sedimentary structures on the upper slope of the eastern province (Figure 1). Up to a few kilometers in diameter and generally showing a low relief of a few tens of meters, these mud volcanoes or so-called 'mud pies' have been described as surface expressions of deep-seated gas chimneys (Loncke *et al.*, 2004).

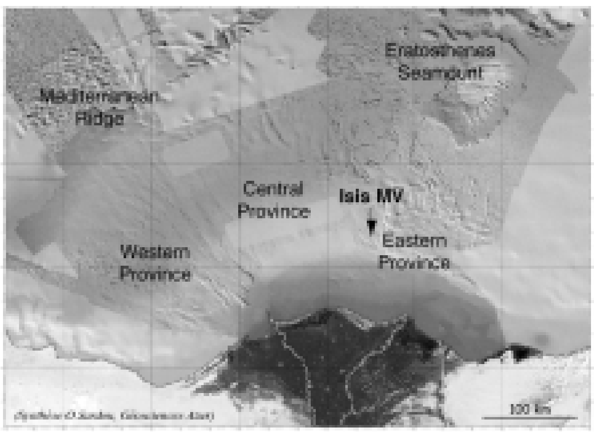

Fig. 1. Bathymetric map of the Nile Deep-Sea Fan and surrounding areas (Sardou and Mascle, 2003, modified).

Isis mud volcano (Isis MV) is located at 32°22' N and 31°23' E at a water depth of approximately 1020 m. In contrast to the more complex structure of the neighboring Osiris and Amon mud volcanoes, Isis MV shows a very distinct camembert-shaped morphology with relatively steep flanks and a gently domed top elevated between 20 and 40 m above the surrounding seafloor

(Figure 2). During the Nautinil expedition in 2003, Isis MV was explored in detail for the first time using the French submersible 'Nautile'. In addition to numerous surface sediment temperature measurements conducted in the course of two dives of the submersible, two gravity cores were recovered from the center of the mud volcano and sediment temperature measurements were obtained at the same time by using outrigger probes mounted on the gravity corer. Temperatures of more than 40 °C at 10 m below the seafloor indicated an exceptionally high level of activity and led to another visit to this mud volcano in 2004. During the Mimes expedition, Isis MV was the site of a particular focus of sediment temperature measurements and geochemical pore water analysis. A total of eight cores of which seven were combined with *in situ* temperature measurements, helped to shed new light on the internal structure and activity of this mud volcano. The results of sediment temperature measurements and geochemical pore water analysis have been combined to provide a three-dimensional insight into the recent activity of the mud volcano and to constrain a coupled thermal and geochemical transport model.

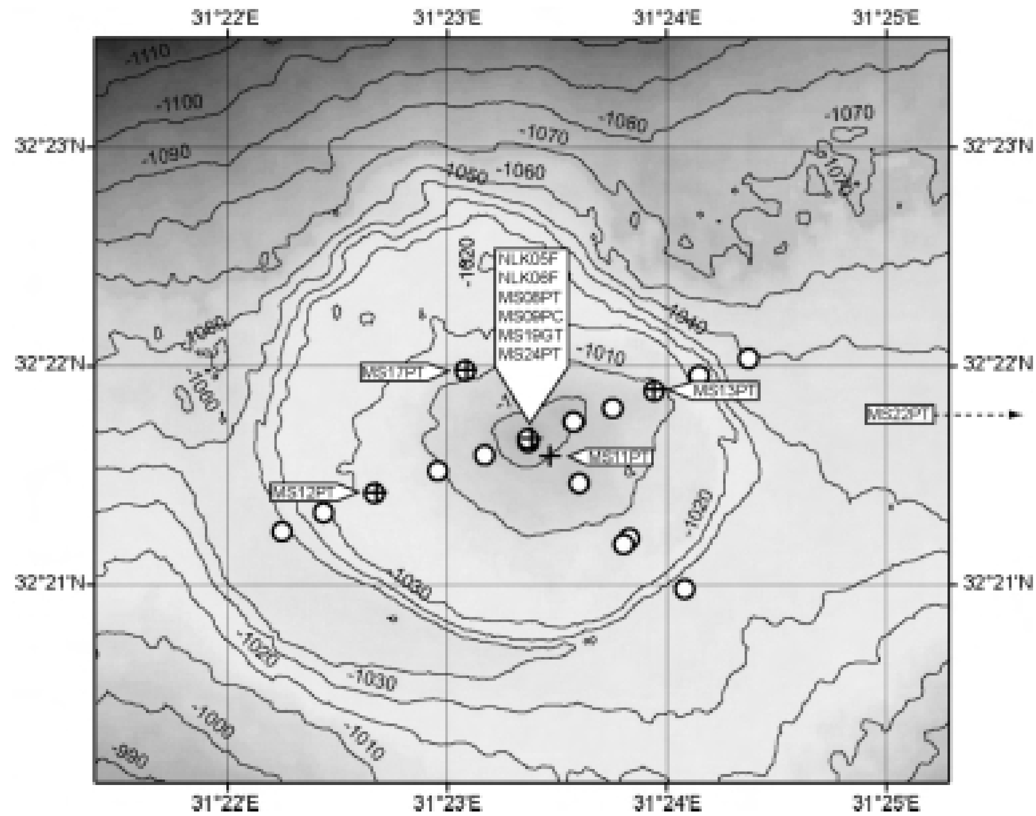

Fig. 2. Surface temperature measurements (circles) and gravity/piston corer stations (crosses) on Isis MV during the Nautinil and Mimes expeditions (bathymetric data courtesy of S. Dupré).

GEOTHERMAL OBSERVATIONS

In the course of the Nautinil expedition in September 2003, sediment temperatures were measured at depths of 0.3 and 0.59 m below the seafloor at 17 stations on Isis MV during two dives of the submersible 'Nautile' (Figure 2). While the surface temperature gradient a few meters away from the flank of the volcano was 0.004 °C/m, the gradients measured on the plateau were greater than 0.02 °C/m and showed a distinct peak of 2.28 °C/m at the center of the mud volcano. Where two more sediment temperature profiles measured with outrigger probes attached to the gravity corer revealed even higher gradients of up to 2.78 °C/m at depths between 2 and 7 m and showed a slightly convex-upward shape (Figure 3).

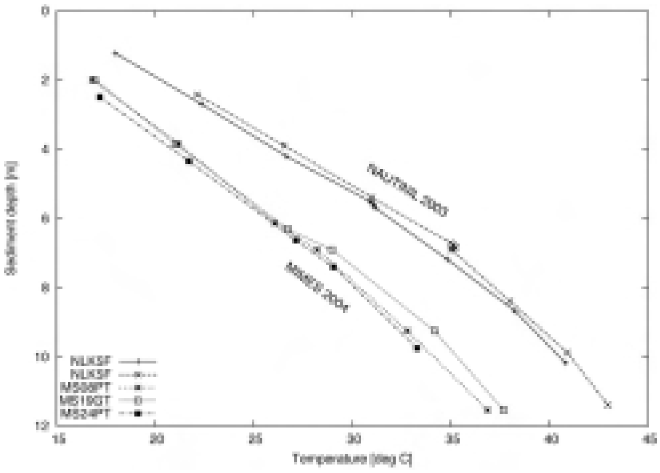

Fig. 3. Temperature profiles recorded at the center of Isis MV during the Nautinil and Mimes expeditions.

During the Mimes expedition in June/July 2004, sediment temperature profiles were measured again using outrigger probes mounted on the piston and gravity corers for three stations in the center of Isis MV and four additional locations on the top of Isis MV at different distances from the center (Figure 2). Compared to the temperature profiles recorded during Nautinil, just nine and a half months earlier, the sediment temperatures measured at the center had decreased by more than 5 °C at approximately 7 m below the seafloor. The previously observed convex-upward curvature of the profiles had disappeared and the temperature gradient did not exceed 2.3 °C/m, corresponding to a decrease in heat flow of about 17 percent. However, the temperature profiles obtained at the center and at the four stations at different distances from the center confirmed the distinct peak measured during the Nautinil expedition and revealed an axisymmetric structure of the mud volcano.

Pore water chloride profiles

One of the two gravity cores recovered from the center of Isis MV during the Nautinil expedition was sampled for geochemical pore water analyses. As illustrated in Figure 4, the chloride profile for NLK6F shows a rapid decrease from the seawater concentration of about 608 mmol/kg to less than 170 mmol/kg within the uppermost meter of the core. The pore water chlorinity remains low at values between 150 and 180 mmol/kg until a depth of approximately 7 m below sediment surface, from where the concentration increases again slowly with depth, reaching 285 mmol/kg at the lower end of the core.

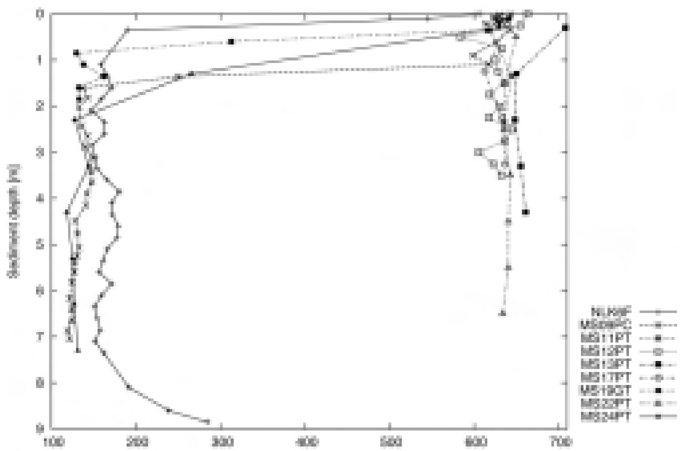

Fig. 4. Pore water chloride profiles measured on cores recovered during the Nautinil and Mimes expeditions from Isis MV and a reference site.

The pore water chloride profiles of seven more cores from Isis MV obtained during the Mimes expedition are also shown in Figure 4. All three profiles from the center (MS09PC, MS19GT, MS24PT) show seawater chloride concentration within the upper few tens of cm of the core, followed by a sharp decrease with depth to values of less than 160 mmol/kg. The chlorinity remains low until the lower end of the core. Unfortunately, even though both the observed mud smear on the piston and gravity corers and the temperature measurements obtained from outrigger probes indicated penetration depths of more than 12 m, the sediment cores from Isis MV recovered during the Mimes expedition did not exceed a length of 7.3 m. Consequently, the new cores did not yield any information on the lower transition zone towards higher chloride concentrations found at the core NLK6F from the Nautinil expedition. The pore water profiles obtained from the four additional stations on the top of the mud volcano (MS11PT, MS12PT, MS13PT, MS17PT) show more or less the same chloride concentrations as the reference profile (MS22PT) measured at a station uninfluenced by the mud volcano activity, although the variability is greater. Unlike the corresponding temperature profiles, they do not show a gradual change with distance from the center.

GEOTHERMAL AND GEOCHEMICAL TRANSPORT MODEL

If the geochemical data are neglected, the convex-upward curvature of the temperature profiles measured at the center of Isis MV during the Nautinil expedition could be explained by upward flow of hot fluids (Bredehoeft and Papadopulos, 1965). Consequently, the observed change from convex-upward to linear temperature profiles along with the decrease of sediment temperatures between the Nautinil and Mimes expeditions could be interpreted as a decrease of upward fluid flow at the center of the mud volcano. For this interpretation, models not shown here suggest a flow rate of approximately 0.6 m/a for the time of Nautinil and less than 0.2 m/a for the time of Mimes. However, the increase of chloride concentration below 7 m observed in the core NLK6F from the Nautinil expedition (Figure 4) and the more or less concave upward shape of this lower part of the chlorinity profile seems incompatible with the assumption of upward fluid flow.

A conceptual model that may explain both the geothermal and the geochemical observations is the deposition of a mud flow characterized by a relatively high temperature and low pore water chlorinity. Upon the deposition, both the temperature and the low pore water chlorinity of the fresh mud would slowly adjust to the temperature and chlorinity of the seawater at the top as well as to the temperature and pore water chlorinity of the sediments covered by the mud flow. Consequently, both the geothermal and the geochemical profile would contain information about the age of the mud flow. However, since the conduction of heat in the sediments is about three orders of magnitude faster than the diffusion of chloride in the pore water, the disturbance in the temperature profile caused by the fresh mud flow would equilibrate much faster than the corresponding anomaly in the pore water chloride profile.

In order to verify this interpretation, the finite elements software FEMLAB 3.1 was applied to develop a combined one-dimensional geothermal and geochemical transport model for a sediment column at the center of Isis MV. The model is based on the assumption that heat transfer is controlled by conduction and that the transport of chloride in the pore water is dominated by diffusion, while advective heat or mass transfer is neglected. Both transport processes are coupled through a temperature-dependent definition of the chloride diffusion coefficient given by D=(T*0.24+4.7)*1e-10, where D is the diffusion coefficient for chloride [m^2/s] and T is the temperature in °C (Li and Gregory, 1974). The thermal diffusivity of the saturated sediment is assumed to be 2e-7 m^2/s and the initial temperature of the fresh mud flow is estimated at 37°C at the time of expulsion.

The model domain represents a sediment column from 0 to 14 m below the seafloor and is subdivided into 140 elements, yielding an homogeneous element size of 0.1 m. For the geothermal part of the model, the upper boundary condition at the sediment/seawater interface is the constant bottom water temperature of 13.8 °C, while the lower boundary condition at a depth of 14 m is a constant temperature gradient of 1.9 °C/m as derived from the temperature profiles measured during the Nautinil and Mimes expeditions. The geochemical boundary conditions are given by constant seawater chloride concentration both at the top and at the bottom of the modeled sediment column. This implies that the chloride concentration in the covered sediment was at equilibrium with seawater before the deposition of the fresh mud flow. Since the lower transition zone from low chlorinity within the fresh mud to seawater chlorinity in the covered sediments created by diffusive mixing would be symmetric, it follows that the fresh mud flow would have a thickness of approximately 9.4 m.

The transient equations describing heat transfer by conduction and chloride transport by diffusion are solved simultaneously. For all model runs, the time step is limited to a maximum of one month.

MODEL RESULTS

The first simulation is based on the assumption that the fresh mud flow was deposited instantaneously two years before the first observations during the Nautinil expedition. The pore water chloride profile and sediment temperature profiles after two years of equilibration with the seawater at the top and the covered sediments at the bottom are illustrated in Figure 5. The agreement between the modeled chlorinity profile and the measured concentrations is relatively good for the upper transition zone at the sediment/seawater interface, but the modeled transition at the boundary between the fresh mud and the covered sediments does not fit the measured chloride concentrations, suggesting that the time required for this transition zone to develop was more than two years. The modeled temperature profile is curved more strongly than the measured profiles, which also indicates that more time is required for equilibration.

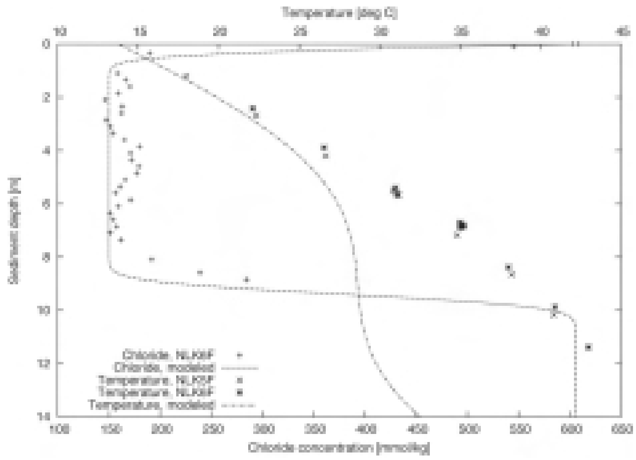

Fig. 5. Model results for an instantaneous deposition of a mud flow two years before the Nautinil expedition.

For the second simulation, the time between the instantaneous deposition of the fresh mud flow and the first observations during the Nautinil expedition was increased from two to ten years. Figure 6 shows that the agreement between the modeled pore water chlorinity and the measurements for the Nautinil core NLK6F is very good at the lower transition zone, but poor at the upper transition zone. It can be seen that the modeled temperature profile for ten years after the deposition of the mud flow is linear and therefore completely at equilibrium with the imposed boundary conditions, indicating that the observed temperature changes between Nautinil and Mimes would not be reflected by the model.

The two model results described above led to a third simulation based on the idea that the mud flow was not deposited instantaneously but over a longer period of time. Assuming that the deposition of the fresh mud flow started 10 years before the time of the Nautinil expedition and continued for a total of eight years yields the simulation results illustrated in Figure 7a. For the pore water chloride profile at the time of the Nautinil expedition, both the relatively sharp upper

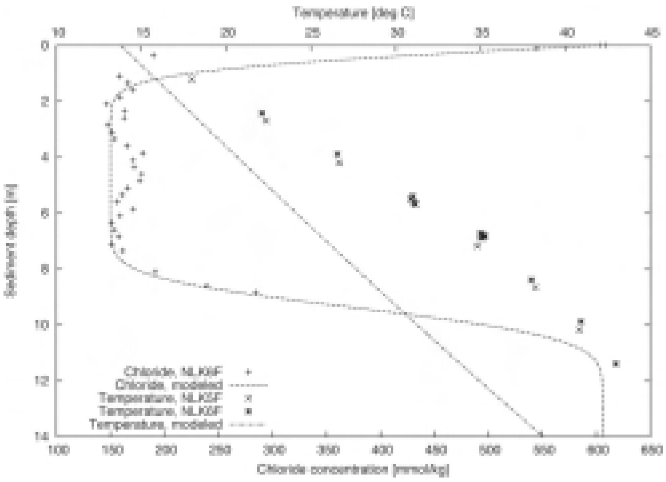

Fig. 6. Model results for an instantaneous deposition of a mud flow ten years before the Nautinil expedition.

transition zone and the broader transition zone at the boundary between the fresh mud and the covered sediments are well represented in the model. The modeled temperature profile for the same time also fits the measurements. However, for the time of the Mimes expedition (Figure 7b), the modeled temperature profile is much too hot and the curvature is stronger than observed.

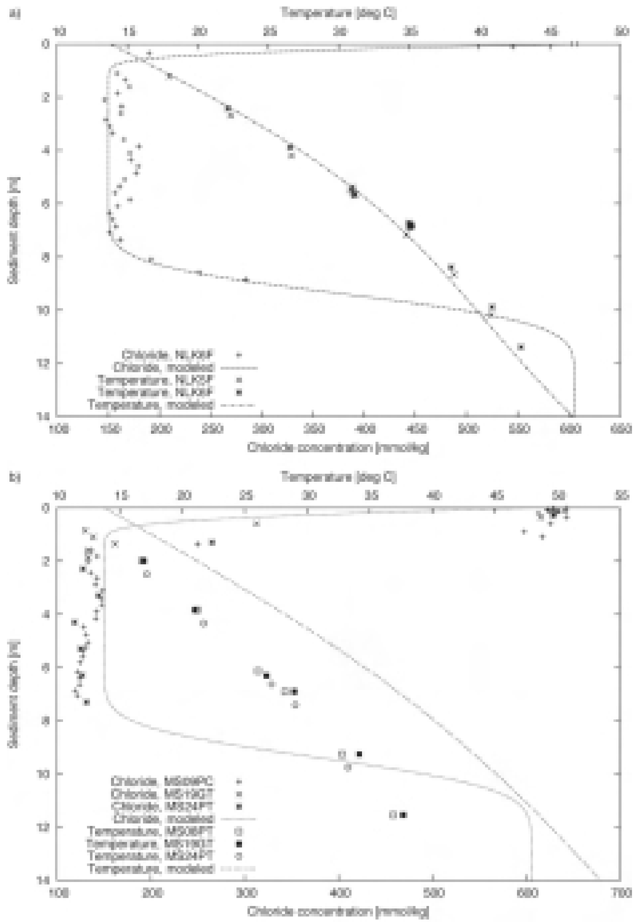

Fig. 7. Model results for continuous deposition of a mud flow from ten years until two years before the Nautinil expedition. **a**) Nautinil; **b**) Mimes.

None of the simulations described above yields a pore water chloride profile that agrees with the measurements for the cores recovered during the Mimes expedition. In fact, the step in the upper parts of the observed chloride profiles cannot be explained by simple diffusive mixing but requires an additional mixing process much faster and much more efficient than diffusion. This need for an additional mixing process is supported by the temperature profiles measured during the Mimes expedition, because linear extrapolation reveals that the bottom water temperature of 13.8 degrees can be expected already at a depth of approximately 1 m below the seafloor. However, there are presently no data that may be used to characterize this effect. As a first approach, the set-up of the previous simulation was modified in such a way that after the first observations during the Mimes expedition, both the chloride diffusion coefficient and the thermal diffusivity of the saturated sediment were increased by two orders of magnitude for the upper meter of the model domain in order to represent the more efficient mixing process required. As illustrated in Figure 8, both the modeled chloride profile and the modeled temperature profile fit the measurements much better than the previous simulations, even though the modeled temperature profile is still too hot and not linear enough.

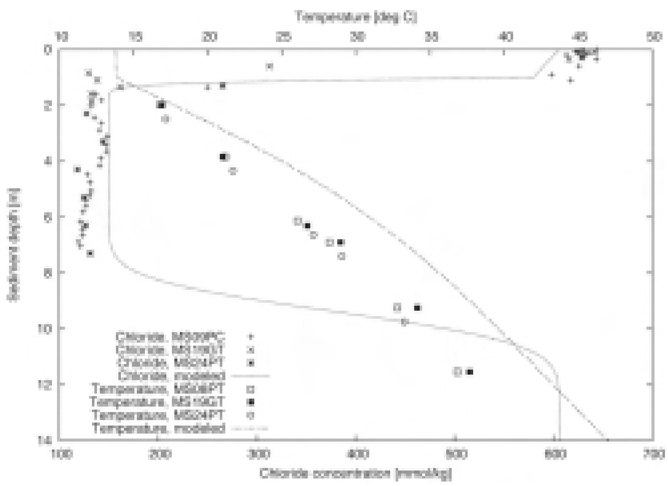

Fig. 8. Model results for continuous deposition of a mud flow from ten years until two years before the Nautinil expedition and additional mixing within the uppermost meter of the sediment column after the time of the Nautinil expedition.

CONCLUSIONS

The simulations presented here demonstrate that the sediment temperature profiles and pore water chloride profiles measured at Isis MV during the Nautinil and Mimes expeditions may be explained in general by the deposition of a fresh mud flow, which is characterized by a relatively high initial temperature and low pore water chlorinity. The best results are obtained by assuming that the mud flow was not deposited instantaneously but over a longer period of time, even though the modeled temperature profile for the time of the Mimes expedition is too hot and curved much more than the observed profile. This suggests that the equilibration time for the heat transfer in the model is too short, even though the modeled chloride profile for the same time seems to agree with the measurements. This discrepancy between the model and the measured temperatures might be explained if the fresh mud flow was not deposited continuously as a single event, but rather as a sequence of episodic mud flows over the same period of time. Interruptions of the mud deposition for periods in the order of one year would allow for significant cooling of the fresh mud while the effects on the chloride profile would be small.

The step observed in the upper parts of the pore water chloride profiles of the cores recovered during the Mimes expedition as well as the corresponding temperature observations require the presence of an additional mixing process that transports both the temperature and the chloride concentration of the seawater to a depth of approximately 1 m below the seafloor. However, this process has not yet been identified.

More detailed geothermal and geochemical observations are needed for a better understanding of the recent activity of Isis MV. Pore water analyses of longer cores would be particularly useful, as the data presently available are insufficient to verify simulation results for depths of more than 7.3 m below the seafloor. In addition, long term observation of the temperature profile would help to constrain models of heat transfer.

Prokaryote-derived morphologies in fossil cold-seep carbonates of the Mediterranean region

Barbara Cavalazzi and Roberto Barbieri

Dipartimento di Scienze della Terra e Geoambientali, Università di Bologna, Bologna, Italy

ABSTRACT

The most typical deposit related to a hydrocarbon seep is the authigenic carbonate derived from microbial activity in anoxic conditions. This activity is at the base of the chemosynthetic food chain established in seep communities. Physical evidence of the interactions between microbial metabolism and seep environment in ancient geologic bodies is present in carbonate accumulations and occurs at various scales, from the outcrop to the micrometer scale. Such evidence can be broadly included in sedimentary and organosedimentary fabrics, morphological fossils, and bioinduced minerals. Fossil prokaryotes and microbialites are mostly concentrated in and around lithofacies directly involved in the seepage, or in mineral products formed during early diagenetic phases. Seep limestone bodies from Morocco (Paleozoic) and Italy (Cenozoic) have provided a wide inventory of these evidences.

INTRODUCTION

While the discovery of cold-seep ecosystems goes back more than 20 years (Paull *et al*., 1984), surprises are not exhausted and the bacteria and clam communities reported from the antarctic deep ocean floor, in areas beneath ice cover for at least 10,000 years, are a compelling example of a recently discovered chemotrophic ecosystem sustained by seepage (Domack *et al*., 2005). Cold-seep ecosystems are common in continental margins worldwide (Campbell, 2005) and their study has significantly expanded our knowledge of extreme environments. Also, they have importance in an astrobiological perspective (Shapiro, 2004), by considering that chemosynthesis can be independent from Earth-like ambient factors, such as light and free oxygen, and methane, the main seeping gas, is abundant in the Solar System.

Cold-seep ecosystems have a long geological history. They are known since at least Silurian time (Barbieri *et al*., 2004) and probably older examples are just waiting somewhere to be discovered. A byproduct of cold-seep environments is the authigenic precipitation of calcium carbonate derived from the increased alkalinity induced by microbial metabolism in anoxic conditions (Ritger *et al*., 1987). Such a biologically induced mineral precipitation may occur at or beneath the seafloor, where the formation of thin crusts, such as those today precipitating in the Adriatic Sea (Figure 1a), may turn into volumetrically large deposits (Figure 1b). These authigenic carbonate accumulations may also form in critical environments, such as below the calcite compensation depth (see the example by Greinert *et al*., 2002). Once embedded or replaced by mineral compounds, the biological components can be preserved and become useful elements for the diagnosis of a fossil cold seep site. Because the chemosymbiotic communities of invertebrates typifying the modern seep ecosystems may be absent in fossil counterparts (see the example described by Aiello *et al*., 1999, 2001), sedimentary and bio-geochemical attributes are also important diagnostic proxies (recent review by Peckmann and Thiel, 2004). The characteristic ^{13}C-depletion of mineral (calcium carbonate) and organic compounds (lipid biomarkers) in modern and ancient methane seeps depends on the microbial ecology established by consortia of methanotrophic archaea and sulfate-reducing bacteria. Activity of methanotrophic and thiotrophic endosymbionts in soft tissues of seep invertebrate communities (clams, mussels and tubeworms), and of the sulfide-oxidizing, mat-forming filamentous bacteria (*Beggiatoa* mats) play a key role in a seep ecosystem, where they are at the base of the food chain.

Physical evidence of the interactions between microbial metabolism and seep environment in ancient geologic bodies are present in carbonate microbialites and other microbial-derived textures, which occur from the scale of the field to the scale of the electron microscopy. These evidences can be summarized in i) sedimentary and organosedimentary fabrics, ii) morphological fossils, and iii) bioinduced minerals. Evidence demonstrates that fossil prokaryotes and microbialites are mostly concentrated in and around authigenic lithologies directly involved with the seepage, such as conduit and vug fills, and products of early diagenetic phases. Seep deposits from the Silurian-Devonian of Morocco and the Neogene-Recent of Italy provide a wide inventory of such evidence, which is the subject of the present paper.

SEDIMENTARY AND ORGANOSEDIMENTARY FABRICS

Typical microbial-induced fabrics of hydrocarbon seep-carbonates from Italy and Morocco include laminated (stromatolitic) fabrics, organic/mineralized crusts and rims, microtufts, dissolution surfaces, clotted and/or peloidal textures, botryoids, rhombs and spherulitic textures. Finely laminated stromatolitic fabrics have been described in modern methane seep-carbonate crusts, at nearly 5,000 m water depth in the Aleutinian accretionary margin (Greinert *et al*., 2002), and in fossil carbonate accumulations. From remains of the El Borj body, the oldest known fossil cold-seep ecosystem located in the Moroccan Meseta (Barbieri *et al*., 2004), laminated fabrics are present in a well developed stromatolitic and stromatactoid facies (Figures 2a, b). Fine laminae arranged as a stromatolitic fabric have been found in the Early and Middle Devonian Kess-Kess mounds of Anti-Atlas, Morocco (Cavalazzi and others, unpublished data), where they line veins and sills crosscutting these spectacular conical mounds (Figure 2c). In spite of a suggested hydrothermal origin for the Early Devonian Kess-Kess mounds, low $\delta^{13}C$ values (Cavalazzi and others, unpublished data) and the mineral fluid inclusions (Belka, 1998) measured from veins and sills infill, demonstrate that they also acted as conduits for cold fluid (including methane) advection. In only one conical mound, the Middle Devonian Hollard Mound, worm-tube and bivalve fossils (Figure 3), associated with geochemical evidence suggest a seep-derived origin (Peckmann *et al*., 1999; Peckmann *et al*., 2005).

Mineralized crusts and encrusted horizons, possibly with some organic remnants, are common sedimentary features of seep carbonates (Figure 4). The nature of these features depends on the local ambient chemistry, which is largely established by microbial consortia. Crusts can derive from rapid mineral precipitation, such as the authigenic iron oxide concentrations of the El Borj body (Figure 4a), or from early mineral replacement of organic (microbial) compounds during a process of biologically induced mineralization, which is extremely common for bacteria (Lowenstam, 1981). Mineral rims of microbial origin can also coat seep megafaunal remains, such as the tubeworms encrusted by nondetrital micrite described by Campbell *et al*. (2002) from a Cretaceous seep limestone of California. Sharp changes in physico-chemical gradients can also be documented by dissolution/corrosion patterns on skeletal and sedimentary surfaces (Figure 4b). Microtufts are microbial-derived aggregates that concentrate ferric iron minerals in micritic facies. The only described paleoseep with abundant microtufts is the Silurian-aged El Borj body (Figure 4c), where they are associated with other iron concentrations.

Another type of microcrystalline aggregates leads to the formation of the “clotted micrite” (Figure 4d), which consists of irregular microaggregates cemented by calcite spar (Peckmann *et al*., 2002) or micrite, having a typical microbial origin. Clotted fabrics are largely reported from modern and ancient seep deposits, and are present in authigenic carbonates regardless of proximity to seep conduits. Peloidal fabrics would likely have the same origin of the clotted micrite.

Despite compaction and early cementation processes, a cold-seep limestone can preserve some original porosity. In the Miocene Pietralunga methane-seep deposit of northern Apennine, for example, cavities and vugs are rimmed with carbonate cements and still partially empty. These empty parts are almost totally filled with clusters of zoned spherulites and rhombs (Figures 5a, c) composed of alternations of calcium carbonate and dolomite. For these spherulites and rhombs, a microbial origin (sulfate-reducing consortia) has been suggested by different lines of evidence (Barbieri and Cavalazzi, 2005), including their association with aragonite botryoids and splays cements (Figure 5d), and the local presence of minerals that can be explained in terms of biological (microbial) intervention. Although with a different development and compositional combination, spherulites have been described from other Miocene paleoseep carbonates of Italy (Terzi *et al*., 1994; Cavagna *et al*., 1999; Peckmann *et al*., 2004). The same microbial-related origin has been also hypothesized for the large dolomite rhombs of the Kess-Kess veins and sills (Cavalazzi, unpublished data). These rhombs are often associated with stromatolitic microfacies and have a characteristic zoned organization consisting of mineral and organic alternations (Figures 5e, f).

MORPHOLOGICAL FOSSILS

The expression "morphological fossil" is here used for all morphologies that can be directly traced back to their biological origin. Preserved bacterial fossils as cells or cell colonies are rare in fossil seep ecosystems. Putative cocci and bacterial rods are reported by Shapiro (2004) from the Cretaceous Tepee Buttes of Colorado, and have also been recovered from the Pliocene Stirone seep deposit of northern Apennine (Figure 6). The recognition of biogenicity for the bacterial fossils is still an issue under discussion. In general, because of the micrometer-size and simple shape of morphologies that mimic bacterial cells, a clear origin (mineral or biological) is rarely obvious (see discussion in Westall, 1999).

A spectacular finding of bacterial cell colonies is from the Pietralunga seep deposit (Barbieri *et al*., 2001; Peckmann *et al*., 2004; Barbieri and Cavalazzi, 2005). In this carbonate mass, dense to loose clusters of dark filaments with 1-3 mm length and about 100 µm diameter, are distributed in the micritic groundmass, associated with aragonite cements, and with a mat-forming arrangement (Figures 7a, b). These filamentous structures have been interpreted as exceptionally well preserved, giant sulfide-oxidizing bacteria belonging to the family Beggiatoaceae, that in modern seep environments, such as in the Gulf of Mexico (Larkin and Henk, 1996), develop typical bacterial mats. The Beggiatoaceae genus *Beggiatoa*, for example, is amongst the largest of prokayotes and can range in diameter up to nearly 200 µm (Larkin *et al*., 1994). *Beggiatoa* mats originate as a consequence of the upward migration of hydrogen sulfide/hydrocarbon-rich fluids. Bio-geochemical support for interpreting filaments of the Pietralunga paleoseep as giant bacteria was convincingly provided by Peckmann *et al*. (2004). An example of non colonial bacterial fossils are the micrometer-size, filamentous morphologies (Figure 7c) recovered in the authigenic micrite of the stromatolitic textures lining veins and sills (Figure 2c) of the Kess-Kess mounds (Cavalazzi *et al*., unpublished data).

The most common microbial morphologies recovered in cold seep deposits are mineralized bacterial sheaths or generic biofilm textures. This is because bacterial cell colonies are commonly encased in protective exopolymeric substances (EPS) biofilms, which often undergo early mineralization processes. Simple sheaths of microbial origin binding and trapping biodetrital or siliciclastic grains in the Stirone paleoseep (Figure 8) are significant examples. Complex structures interpreted as remains of mineralized bacterial mats have been recently documented in the fossil record. From the Silurian seep limestone of El Borj a three-dimensional alveolar network made up of hematite and filled by calcium carbonate (Figure 9a) has been interpreted as the fossil analogue of mats of filamentous bacteria (see discussion in Barbieri *et al*., 2004). In this example the mineralization by hematite of partially degraded bacterial mats precedes (or co-occurs with) the precipitation of the authigenic carbonate. Similar three-dimensional structures have also been described from Mg-calcite mineral phases that fill and rim cavities and conduits

(Figure 9b) used by fluids migration in the Pliocene Stirone seep (Barbieri and Cavalazzi, 2005). In both the above examples the early mineral replacement by hematite (El Borj) or Mg-calcite (Stirone) of alveolar organic textures is a necessary prerequisite for their preservation.

MINERALS

Authigenic carbonate-group minerals, such as Mg-calcite, aragonite and dolomite, are peculiar of paleoseep sites. Mineral composition of limestone seep bodies, as well as their stable isotope values, may change significantly, depending on the nature of the fluid flow and its interaction with the local environment (Campbell *et al*., 2002). Aragonite, in the form of botryoidal splay texture, and dolomite, in the form of spherulites, abound as cement. Their relationship with microbial processes has been documented in seep environments for aragonite (Aharon, 2000), and with presence of sulfate-reducing bacteria for dolomite formation (Vasconcelos *et al*., 1995). Changes in the chemistry of the expelled fluids may also determine the precipitation of minerals other than carbonates. Barite (Figure 10a), for example, in another authigenic mineral typifying cold seep sites. Its precipitation depends on the amount of barium contained by seeping fluids and on the biogeochemical conditions established by the microbial oxidation of methane (Aloisi *et al*., 2004a).

Iron-based minerals, such as pyrite and hematite, also precipitate in seep environments under microbially controlled conditions. Pyrite is an authigenic mineral that may be abundant in zones of bacterial sulfate reduction. There, sulfide may combine with iron and precipitate pyrite as small globules (framboids, Figure 10b) or pseudomorph of foraminiferal tests (Figure 10c). The interactions between the activity of microorganisms and the hematite precipitation in a cold-seep ecosystem have been described in detail in the Silurian body of El Borj, Morocco (Barbieri *et al*., 2004), where this iron oxide replaced complex organic morphologies or accumulated via intracellular biomineralization.

CONCLUDING REMARKS

Permanent record of microbial activity in the carbonate products of seeps is largely concentrated in (although not limited to) conduit openings and other vugs, and surrounding lithofacies. This depends on the tight relationships between seeping fluids, microbiological activity, and calcium carbonate precipitation. Textures with bacterial imprints are diverse and testify to a life based on chemosynthesis for which compelling examples include the giant *Beggiatoa* of the Miocene seep of Pietralunga (Northern Apennine) and the hematitized, complex microbial networks of the Silurian seep of El Borj (Morocco). In spite of the importance of microbial activity in the formation of authigenic carbonate, biomineralized microbial textures are minor components relative to the overall volume of a seep-carbonate body.

Among the geological contexts strongly suggesting the joint occurrence of chemosynthetic communities of microorganisms and seep (or vent) settings, the Devonian Kess-Kess mounds (Morocco), for which a controversy on their origin is still waiting for a solution, deserve a special interest. In the veins and sills that crosscut these conical mounds and connected deep and seafloor paleoenvironments, geomicrobiological and geochemical (stable isotope) data suggest that the subsurface microbial communities were independent of light and free oxygen. This allows outline hypotheses based upon chemosynthetic processes developed by hydrocarbon (and other fluids)-feeding microbial consortia and able to expand views on the presence and requirements of life on Earth**.** Such adaptation to environments well below the seafloor would characterize a peculiar seep microbiotic community with considerations on the presence of microbial life on other planets. Microbiological studies conducted on modern analogues of the Kess-Kess (and similar) mounds, especially on their internal organization and the relationships between precipitating minerals and microbes, would provide clues for a proper understanding of these (present and past) ecosystems.

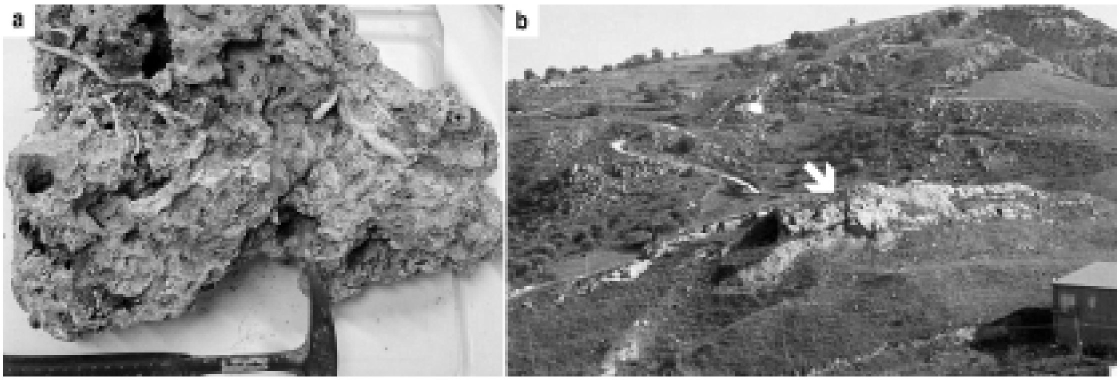

Fig. 1. **a**: Authigenic carbonate crust, Recent, northern Adriatic Sea. **b**: The calcium carbonate accumulation of Roccapalumba, Lower Miocene, Sicily.

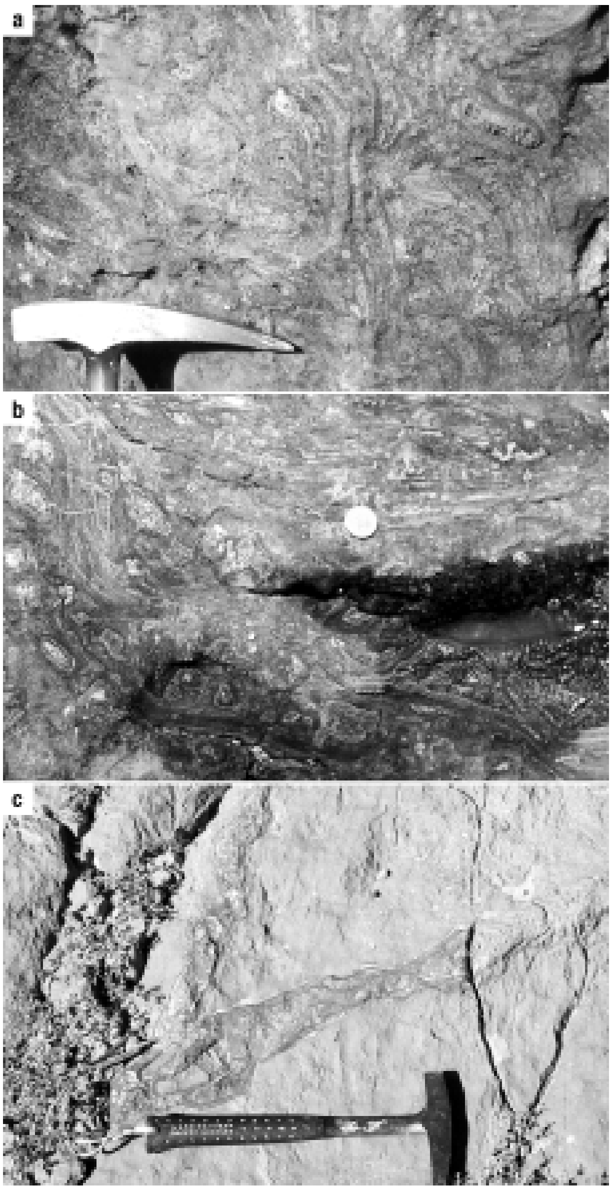

Fig. 2. Stromatolites (**a**) and stromatactoid structures (**b**) of the paleoseep at El Borj, Silurian, Middle Atlas, Morocco. **c**: veins with stromatolite infill from the side of a Kess-Kess conical mound, Devonian, Anti-Atlas, Morocco.

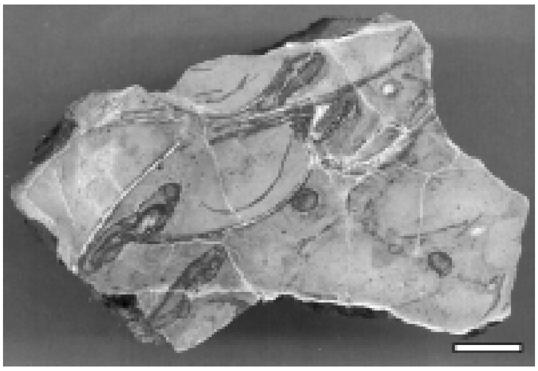

Fig. 3. Megafauna (bivalves) from the Kess-Kess mound known as Hollard Mound, Devonian, Anti-Atlas, Morocco. Scale bar = 3 cm.

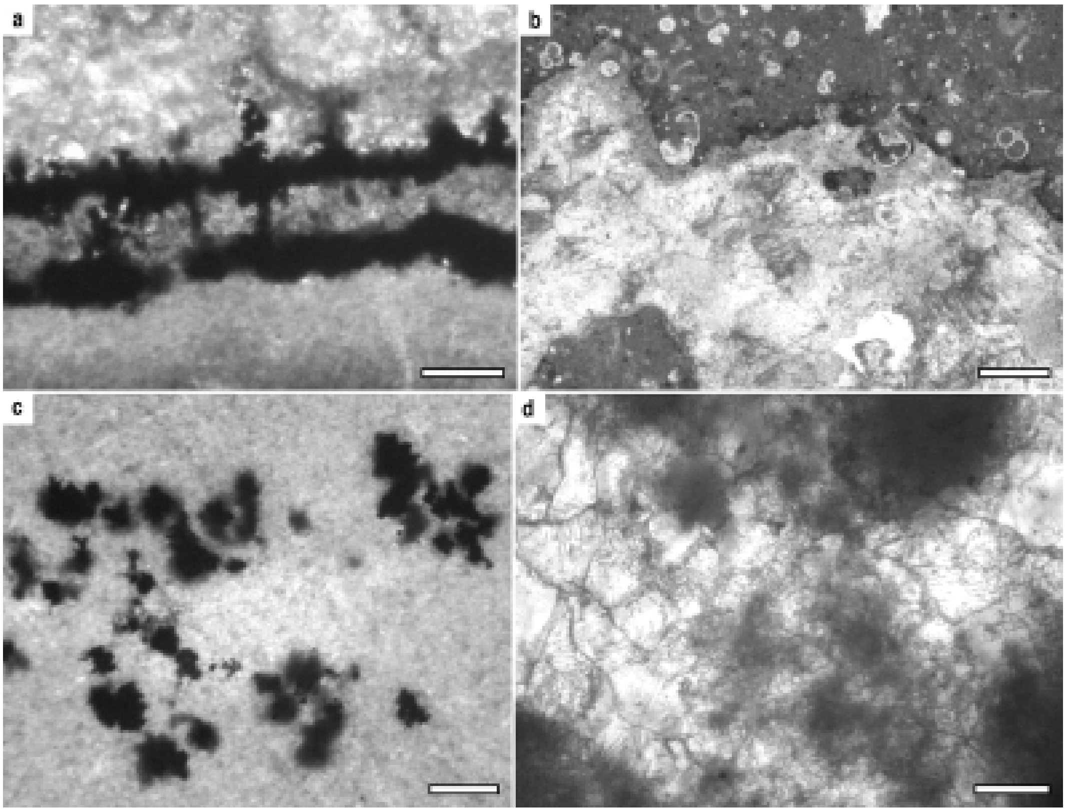

Fig. 4. Transmitted light micrographs. **a**: iron oxide crusts, El Borj paleoseep, Silurian, central Morocco. **b**: boundary (arrow) between authigenic micrite with planktic foraminiferal shells (dark area) and spar infill (light area), Roccapalumba, Lower Miocene, Sicily. **c**: microtufts, El Borj paleoseep, Silurian, central Morocco. **d**: clotted texture, Roccapalumba paleoseep, Lower Miocene, Sicily. Scale bars: **a**, **b**, **c** = 500 μm; **d** = 200 μm.

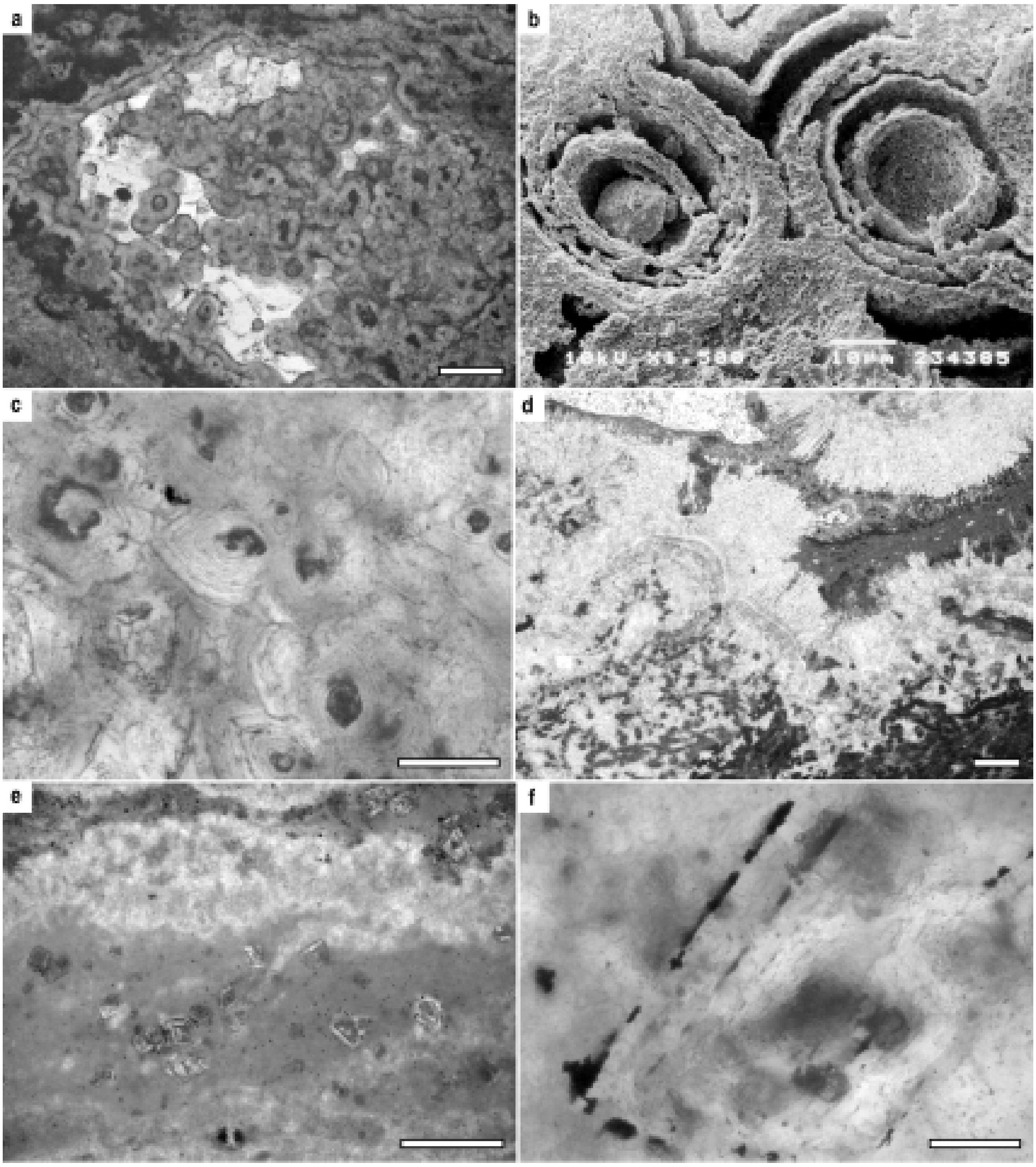

Fig. 5. Spherulite textures from transmitted light (**a**) and SEM (**b**) micrographs, and zoned dolomite rhombs (**c**), Pietralunga paleoseep, Miocene, northern Apennine. **d**: aragonite splays, Pietralunga paleoseep. **e**: dolomitic rhombs embedded in micrite from stromatolites of a Kess-Kess mound, Devonian, Morocco. **f**: detail of a zoned dolomite rhomb from a Kess-Kess mound, note the organic matter (dark) which underlines the zoned fabric. Scale bars: **a** = 50 µm; **b** = 10 µm; **c** = 50 µm; **d** = 1 µm; **e** = 500 µm; **f** = 250 µm. Transmitted light micrographs: **a**, **c**, **d**, **e**, **f**. SEM micrograph: **b**.

Fig. 6. Bacteriomorphs (putative cocci) from the Stirone paleoseep, Pliocene, northern Apennine (SEM micrograph taken by Frances Westall, CNRS, Orléans). Scale bar = 1 µm.

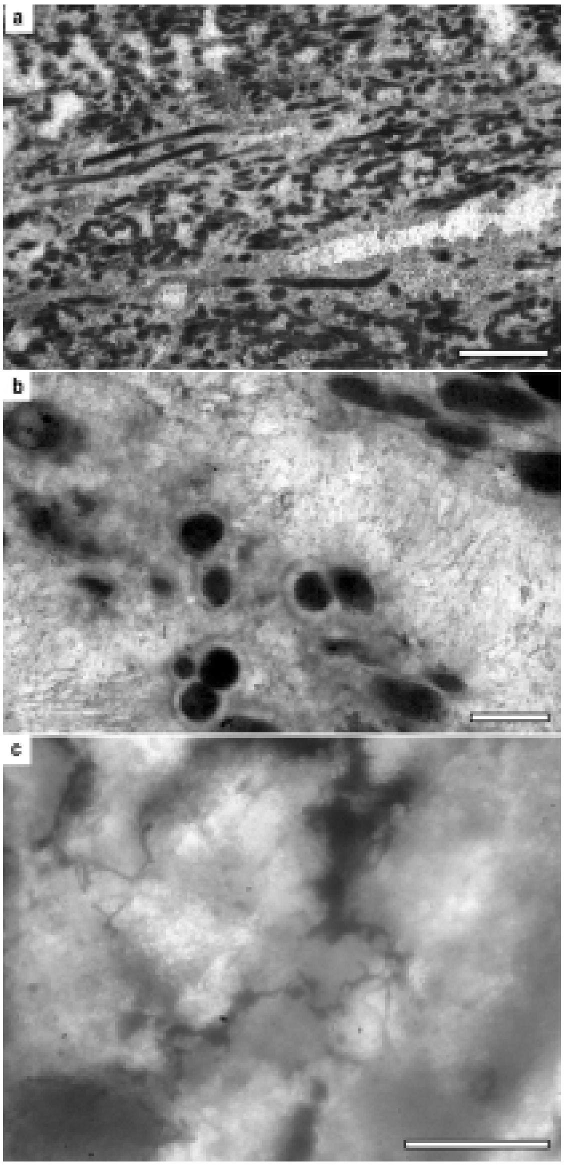

Fig. 7. Transmitted light micrographs. **a**, **b**: dense concentration of filaments arranged as microbial mats and embedded in a microsparite groundmass (**a**), with aragonite cement fringes (**b**), Pietralunga paleoseep, Miocene, northern Apennine. **c**: filamentous morphologies from the stromatolites of veins crosscutting the Kess-Kess mounds, Devonian, Morocco. Scale bars: **a** = 1 µm; **b** = 200 µm; **c** = 50 µm.

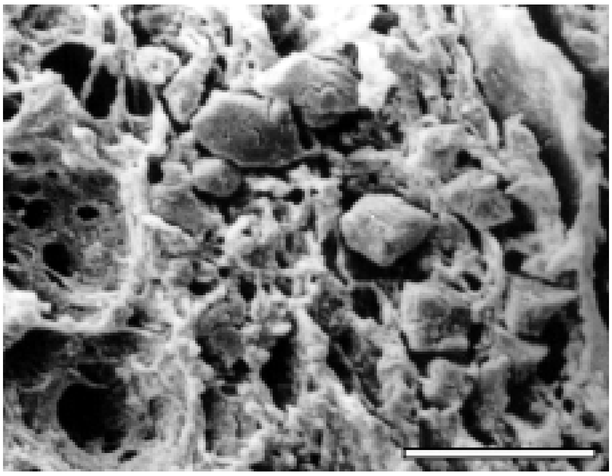

Fig. 8. Siliciclastic grains trapped by microbial sheaths, Stirone paleoseep, Pliocene, northern Apennine, SEM micrograph. Scale bar = 5 µm.

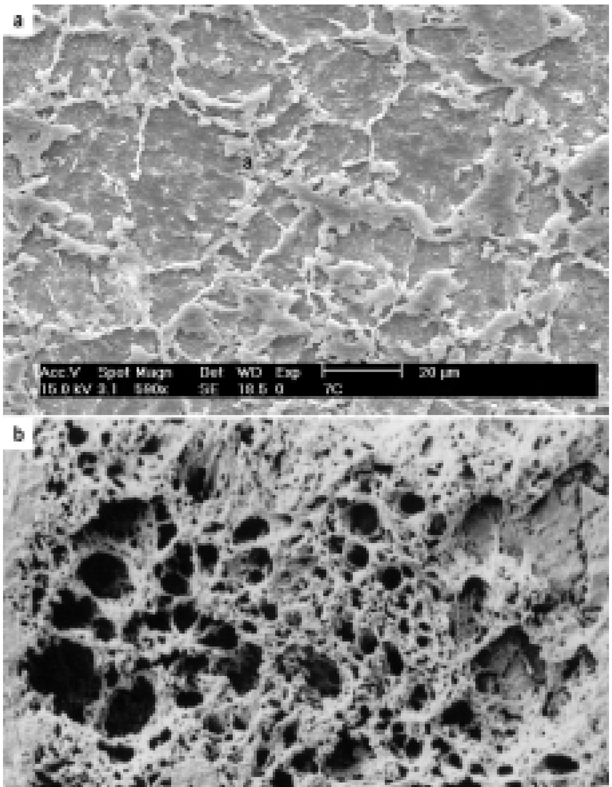

Fig. 9. SEM micrographs of alveolar morphologies described from the Devonian El Borj (a) and the Pliocene Stirone (b) paleoseeps. Scale bars: 10 µm.

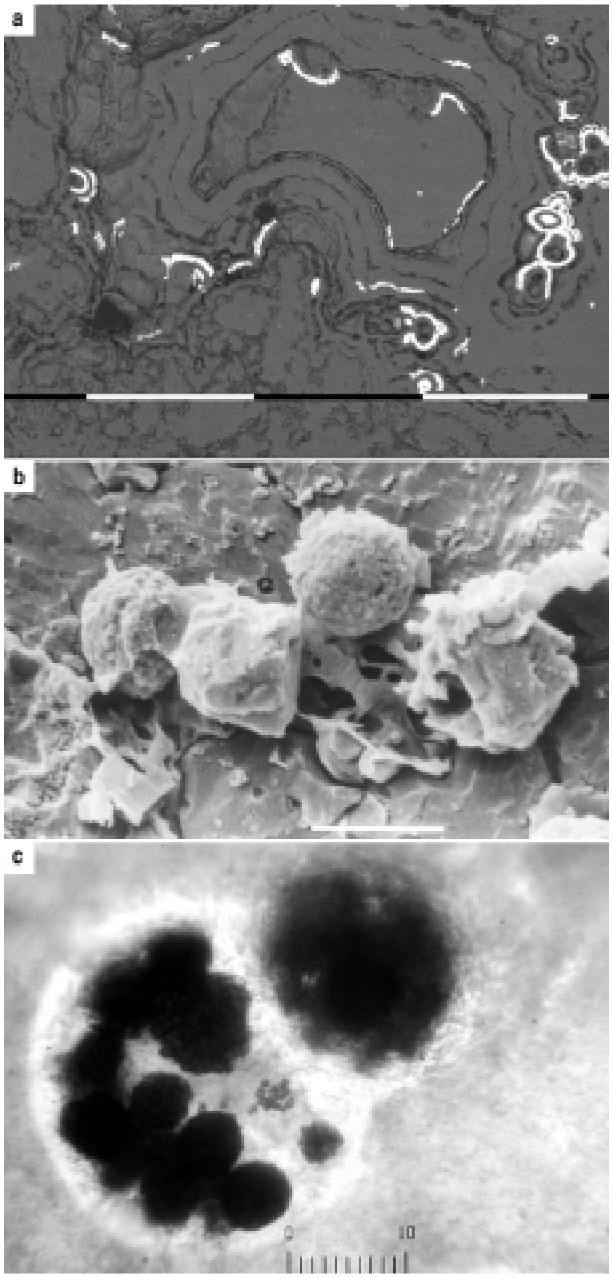

Fig. 10. **a**: SEM micrograph of precipitate barite from the Pietralunga paleoseep, Miocene. **b**: SEM micrograph of pyrite framboids, El Borj paleoseep, Silurian. **c**: Transmitted light micrograph of a planktonic foraminiferal test filled with pyrite framboids, Roccapalumba paleoseep, Lower Miocene. Scale bars: **a** = 100 µm; **b** = 5 µm; **c** = 10 µm.

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IV - LIST OF PARTICIPANTS

Roberto Barbieri	Dipart. di Scienze della Terra e Geologico Ambientali Università di Bologna Via Zamboni, 67 40126 Bologna – Italy Fax +39 051 209 45 22 barbieri@geomin.unibo.it
Germain Bayon	Département des Géosciences Marines IFREMER 29280 Plouzané – France Fax +33 (0)2 98 22 45 70 Germain.Bayon@ifremer.fr
Frédéric Briand *(Director General, CIESM)*	CIESM 16 bd de Suisse 98000 Monaco Fax +377 92 16 11 95 fbriand@ciesm.org
Rossella Capozzi	Dipart. di Scienze della Terra e Geologico Ambientali Università di Bologna Via Zamboni, 67 40126 Bologna – Italy Fax +39 051 209 45 22 rossella.capozzi@unibo.it
Silvia Ceramicola	Istituto Nationale di Oceanografia e di Geofisica Sperimentale (OGS) Borgo Grotta Gigante 42/c 34010 Sgonico, Trieste – Italy Fax +39 040 432 73 07 sceramicola@ogs.trieste.it
Gert J. De Lange	Marine Geochemistry and Chemical Oceanography Faculty of Geosciences Utrecht University Budapestlaan 4 3584 CD Utrecht – The Netherlands Fax +31 (0)3 02 53 53 02 gdelange@geo.uu.nl

Stéphanie Dupré
Vrije Universiteit Amsterdam
Faculty of Earth and Life Sciences
Sedimentology and Marine Geology
De Boelelaan 1085
1081 HV Amsterdam – The Netherlands
Fax+31 20 59 89 941
stephanie.dupre@falw.vu.nl

Tomas Feseker
Alfred-Wegener-Inst. for Polar and Marine Research
Am Handelshafen 12
D-27570 Bremerhaven – Germany
Fax +49 (471) 48 31 14 25
tfeseker@awi-bremerhaven.de

Swanne Gontharet
LOCEAN-IPSL (ex LODYC)
Lab. d'Océanographie et du Climat : Expérimentations et Approches Numériques
Université P. et M. Curie
4, Place Jussieu - Case 100 - Tour 45/55, 5ème étage
75252 Paris Cedex 05 – France
sglod@lodyc.jussieu.fr

Naima Hamoumi
Département des Sciences de la Terre
Université Mohamed V
BP 8844 Poste Agdal
Rabat – Morocco
Fax +212 37 68 27 91
hamoumi@fsr.ac.ma

Jean-Pierre Henriet
Renard Centre of Marine Geology
Department of Geology and Soil Science
Ghent University
Krijgslaan 281 s.8
B-9000 Gent – Belgium
Fax +32 9 264 49 67
jeanpierre.henriet@UGent.be

Caroline Huguen
Géosciences Azur
Observatoire Océanologique
La Darse, B.P. 48
06235 Villefranche-sur-mer Cedex – France
chuguen@wanadoo.fr

Chryssanthi Ioakim
Institute of Geology and Mineral Exploration
Department of Geology and Geological Mapping
70, Messoghion Street
Athens 11527 – Greece
Fax +30 210 7779467
ioakim@igme.gr / cioak@mail.ariadne-t.gr

Ingo Klaucke	Leibniz Institute of Marine Sciences IFM - GEOMAR Wischhofstr. 1-3 24148 Kiel – Germany Fax +49 431 600 2922 iklaucke@ifm-geomar.de
Vasilis Lykousis	Institute of Oceanography Hellenic Centre for Marine Research P.O. Box 712 19013 Anavyssos – Greece Fax +30 22910 76347 vlikou@ath.hcmr.gr
Jean Mascle	Géosciences Azur (UMR 6526) Observatoire Océanologique La Darse, B.P.48 06235 Villefranche-sur-mer Cedex – France Fax +33 (0)4 93 76 37 66 mascle@geoazur.obs-vlfr.fr
Luis Menezes Pinheiro	Dep. Geociencias Univ. Aveiro Campus de Santiago 3810-193 Aveiro – Portugal Fax +351 234 370 605 lmp@geo.ua.pt
Dimitris Sakellariou	Institute of Oceanography Hellenic Centre for Marine Research P.O. Box 712 19013 Anavyssos – Greece Fax +30 22910 76347 sakell@ath.hcmr.gr

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