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Deep-sea survey for the detection of methane at the “Santa Maria di Leuca” cold-water coral mounds (Ionian Sea, South Italy)

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ABSTRACT

The “Santa Maria di Leuca” Cold-Water Coral (CWC) province (northern Ionian Sea) was investigated for the first time to detect eventual occurrence of methane anomalies as a possible indication of hydrocarbon seepage stimulating the coral growth. Most coral mounds have developed in correspondence with tectonic scarps and faults, orthogonal to the southern margin and trending NW-SE, which could be potential sites of gas escape. A visual and instrumental inspection was performed by using a new deep-sea probe equipped with video-cameras, sonar, CTD, methane sensors, and a water sampler. Eight areas were explored by 10 surveys, depths ranging from 380 to 1100 m, for a total of more than 26 h of continuous video and instrumental recording. Sediments were also sampled by gravity corers and analysed in laboratory.

The images allowed to assess distribution, abundance and geometry of the colonies, most of which are developed on morphological highs often characterised by tectonic scarps. All data indicate however the lack of a significant occurrence of methane, both in seawater and sediments. No direct or indirect expressions of gas seepage were recognised on the seabed. Weak methane anomalies were detected only in seawater at the base of some fault-linked scarps, where more reducing conditions and bacterial methanogenesis are possibly enhanced by less water circulation. The faults are not fluid-bearing as previously suggested by high-resolution geophysical signatures. The development of the coral colonies thus cannot be attributed to seeping fluids, but to a favourable physiographic position with exposure to nutrient-rich currents.

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1. Introduction

The occurrence of deep-sea Cold-Water Corals (CWC) is generally linked to the migration and concentration of nutrients carried by oceanic currents (e.g., Freiwald, 2002). It also has been reported that, in hydrocarbon-prone basins, coral banks can develop in correspondence with methane seeps, representing a local source of nutrients (Hovland and Risk, 2003; Hovland, 2005).

CWC are often found on sea-floor elevations called carbonate mounds (Freiwald, 2002). On and around these structures there is often a complex interaction of geological, biological and hydro-geological processes (Kenyon et al., 2003; Huvenne et al., 2005; De Mol et al., 2007; Wheeler et al., 2007).

The “Santa Maria di Leuca” (SML) CWC province (Apulian Plateau, Ionian Sea—Fig. 1) hosts living coral colonies of *Madrepora oculata* and *Lophelia pertusa*, within different geomorphological settings (Savini and Corselli, 2010), and their growth is considered to be stimulated only by oceanographic currents (Taviani et al.,

2005). Previous seismic surveys showed that the offshore Apulian Plateau is characterised by important tectonic dislocations (Aurox et al., 1983, 1985; Merlini et al., 2000; Fusi et al., 2006; Fig. 1). The Apulian margin belongs to the Apulian swell, a NW-SE trending narrow ridge of continental crust, running from central Italy to offshore Greece, which represents the foreland for both the Calabrian and the Hellenic Arc. The Apulian swell is a large anticline that involves about 100 km of lithosphere (Ricchetti and Mongelli, 1980) and is segmented by several parallel normal faults. In its western sector, a system of regularly spaced conjugate normal faults (WNW-ESE oriented) with intervals of 1–2 km and with seafloor displacements of up to 200–300 m (Merlini et al., 2000). These active or subrecent faults might have determined also the high seismicity recognised in the Puglia-Salento region and the adjacent offshore area (Argnani et al., 2001).

The seismic data available in the literature (Aurox et al., 1985; Argnani et al., 2001) were combined with the geomorphological data and with high-resolution seismic-stratigraphic data acquired during the first oceanographic cruise of the APLABES project (Savini and Corselli, 2010), allowing to recognise the close correspondence of the mounds hosting living corals with the fault lines. Since fault planes are often main hydrocarbon

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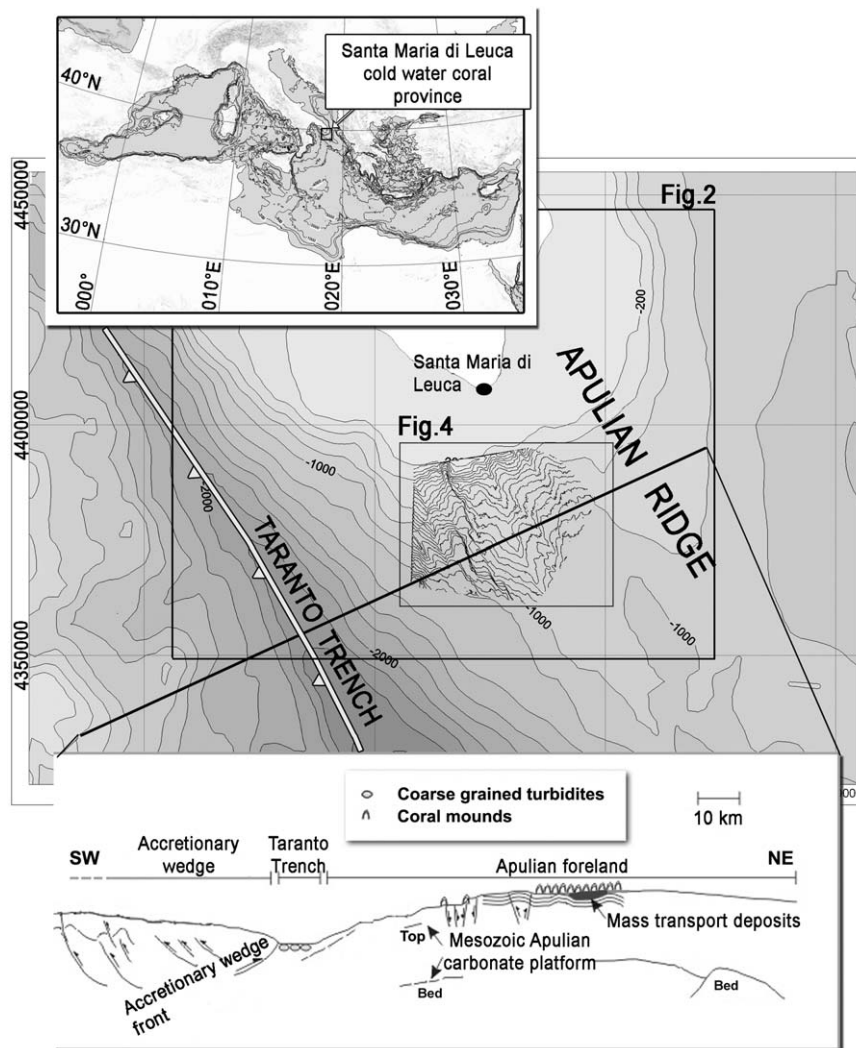


Fig. 1. General map of the northern Ionian Sea showing the investigated area in the Fig. 2 inset (general bathymetry is from GEBCO-97 with contour interval 200 m, and from Savini and Corselli (2010), for Fig. 4 inset) and a brief cross section along the Apennines accretionary wedge and foreland (Apulian swell) with the main tectonic structures that define the regional geology (modified from Fusi et al., 2006). The insets locate the maps presented in the following figures (Figs. 2 and 4).

migration pathways, we checked for the existence of methane anomalies close to the seafloor. The aim was to test if the hypothesis proposed by Hovland et al. (1998), attributing CWC growth to natural gas seepage might be of importance for the SML mounds.

In this study we used a new deep-sea system equipped with a series of tools for visual and instrumental survey and seawater sampling close to the seabed. The system allows sample collection of specific targets and anomalies that were visually observed or detected by the instruments. Beyond getting the first visual images of the coral mounds (as discussed by Rosso et al., 2010; Vertino et al., 2010), the aim was to detect possible direct evidence of seepage (e.g., bubbles, pockmarks) and anomalies of dissolved methane or temperature. Gases were also analysed in the sediments obtained by gravity coring (Fig. 2) during the CNR CORSARO cruise (April 2006) onboard R/V Urania, which was committed for three days to investigate the SML coral province as part of a cooperation between APLABES and HERMES EC project. Also part of the data collected during the CORSARO cruise are two sparker profiles (Fig. 2), which were used to verify the location of faults and to provide useful information about the geology of the investigated area. Geology, physiography and ecosystem of the SML coral mounds are described in other papers of this volume

(Budiillon et al., 2010; Malinverno et al., 2010; Rosso et al., 2010; Savini and Corselli, 2010; Vertino et al., 2010).

2. Methodology

2.1. Visual and instrumental survey

In May 2005 a visual and instrumental inspection was performed with a deep-sea probe, the GAS-SCIPACK module, connected to the MODUS vehicle, towed by the R/V *Universitatis*. The GAS-SCIPACK is an instrumented module for casts and towed surveys (“flyovers”) close to the seabed (Etiope et al., 2005). Originally developed in 2001 for accurate sampling and surveying in deep hypersaline anoxic basins of Eastern Mediterranean Sea (Malinverno et al., 2006), it has been upgraded to host methane sensors, a video overlay system, and to log GPS navigation data. The instrumentation used in the Ionian Sea included two methane sensors (K-METS by Franatech, GmbH, Germany), a CTD and a transmissometer (Idronaut 316 Ocean Seven), 12 Niskin bottles (General Oceanic model 1015 rosette), an echo sounder (Tritech PA500/6), a colour camera and lights (Deep Sea Power & Light

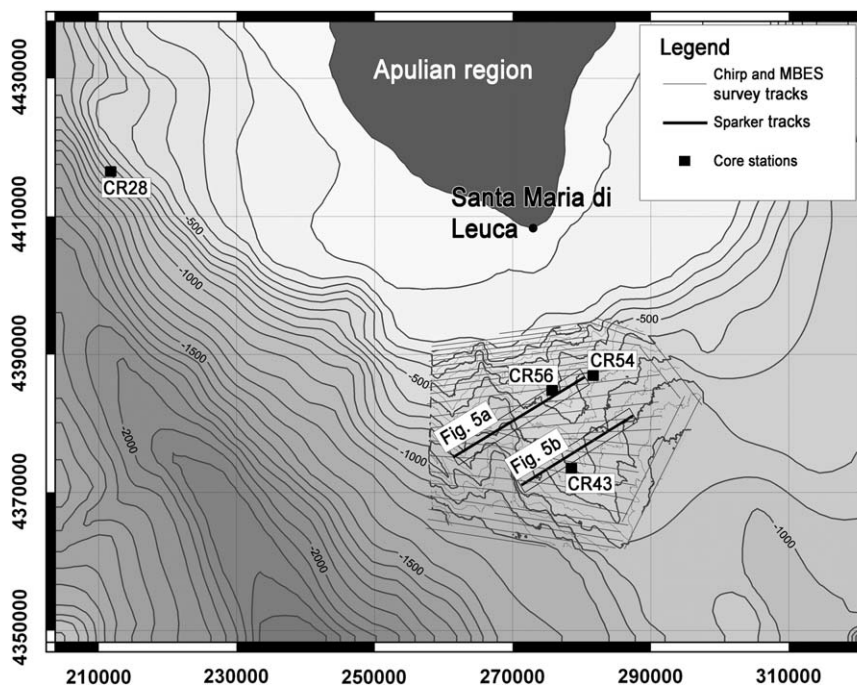


Fig. 2. Location map of sediment cores, high-resolution seismic profiles and sparker lines acquired in the SML coral province (northern Ionian Sea). The insets locate the sparker profiles reported in the Fig. 5a and b.

MULTI-SEACAM 2050 and DL 1040), as well as attitude-sensors for heading, pitch and roll (FSI Ostar compass).

The set-up of the GAS-SCIPACK makes it possible to acquire and refer all measurements to the same clock. This allows one to carry out accurate correlations between different parameters, including those relevant to the system status, like position and attitude. The TV camera ensures a high level of interaction between the surface operator and the phenomena under observation. The GAS-SCIPACK was connected to the MODUS-thrustered vehicle (developed and owned by Technische Fachhochschule Berlin; Fig. 3), a deep-sea shuttle able to carry heavy payload (Gerber and Clauss, 2005). The MODUS also was equipped with video cameras for visual seabed inspection, compass, sonar and altimeter. MODUS, GAS-SCIPACK instrumentation and data transmission are managed, through fiber-optic cabled telemetry, with the NEXUS system and PC control units. Ship movement, MODUS thrusters and winch operations were coordinated to allow slow towing and stops of the system following video-camera images.

The methane sensors (K-METS) are a new fast-response version of semiconductor sensors suitable for casts and areal surveys. Detection limit of the sensors was 50 nmol/l, but lower concentrations of dissolved methane could be recognised as voltage drops as evidenced in laboratory tests and in the field (Christodoulou et al., 2003). The voltage signal is inversely correlated to the methane concentration and variations of 0.1V roughly correspond to about 50–150 nmol/l concentration difference. Laboratory tests showed a response time (T_{90} , time required to reach 90% of final value) of about two minutes. All data, including navigation data from the GPS receiver, were acquired at 2 Hz and logged in ASCII files. Navigation data were also displayed on TV monitors by video overlay.

Eight areas have been explored by 10 surveys (Table 1; Fig. 4), ranging from 380 to 1100 m b.s.l. The investigated areas were selected close to the main sites where previous cruises (Tursi et al., 2004; Taviani et al., 2005) collected living CWC along fault alignments. The dislocations identified on the acoustic geophysical data and mapped from literature were also

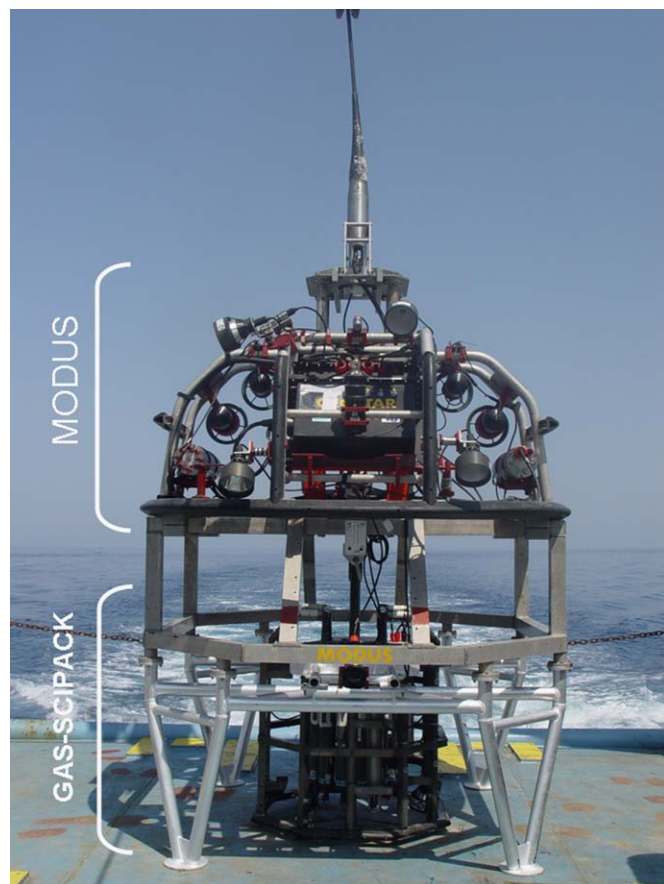


Fig. 3. GAS-SCIPACK and MODUS system onboard R/V Universitatis.

confirmed by the two sparker lines (Fig. 5) acquired during the CNR CORSARO cruise (R/V Urania; April 2006). At these locations several amplitude anomalies were observed in the high-resolution

Table 1
Data of the GAS-SCIPACK instrumental surveys.

	MS1	MS2	MS3	MS3bis	MS4	MS4bis	MS5	MS6	MS7	MS8
Survey coordinates ^a (start-end)	39° 27.296' N 18° 25.298' E 39° 27.643' N 18° 23.789' E	39° 24.461' N 18° 21.484' E 39° 24.767' N 18° 20.856' E	39° 33.106' N 18° 32.138' E 39° 32.914' N 18° 31.501' E	39° 32.827' N 18° 30.994' E 39° 32.858' N 18° 29.510' E	39° 36.761' N 18° 30.571' E 39° 36.696' N 18° 30.378' E	39° 36.463' N 18° 28.150' E 39° 36.513' N 18° 27.511' E	39° 35.858' N 18° 24.027' E 39° 37.347' N 18° 22.636' E	39° 35.207' N 18° 23.350' E 39° 35.015' N 18° 23.379' E	39° 30.748' N 18° 35.736' E 39° 30.807' N 18° 35.671' E	39° 33.269' N 18° 13.279' E 39° 33.316' N 18° 13.292' E
Depth (m)										
<i>Mean</i>	759	1143	790	771	648	629	453	519	906	542
<i>Minimum</i>	729	1102	775	717	631	613	386	495	895	547
<i>Maximum</i>	819	1179	810	804	663	634	498	556	919	539
Seabed distance (m) ^b										
<i>Mean</i>	2.63	2.4	2.4	2.27	2.15	2.24	1.56	2.34	6.8	not recorded
Temperature (°C)										
<i>Mean</i>	13.578	13.647	13.512	13.406	13.496	13.519	13.735	13.643	13.401	not recorded
<i>Minimum</i>	13.547	13.635	13.483	13.377	13.475	13.494	13.659	13.621	13.384	
<i>Maximum</i>	13.609	13.667	13.587	13.445	13.559	13.551	13.828	13.670	13.446	
Salinity (PSU)										
<i>Mean</i>	38.803	38.810	38.826	38.832	38.835	38.839	38.860	38.851	38.843	not recorded
<i>Minimum</i>	38.789	38.795	38.810	38.823	37.886	38.830	38.847	38.828	38.835	
<i>Maximum</i>	38.811	38.834	38.842	38.855	38.862	38.849	38.874	38.859	38.850	
Methane (METS-volt) drops: Δv	< 0.01	–	–	0.01	0.04 0.02	0.02	–	0.02	–	not recorded
Methane (GC-nmol/l) <i>Bottle and CH₄-concentration</i>	1–4.4	1–5.8 2–5.1	1–4.6 2–5.1 3–2.9 4–3.5 5–3.8	1–2.9 2–3.5 3–3.9 4–4.0	1–3.8 2–15.4 3–25.8 4–8.9	1–4.5 2–8.1 3–13.9 4–10.0	1–2.7	1–8.0 2–3.0 3–2.8 4–3.3	1–4.1 2–4.5 3–4.8 4–5.2 5–5.0 6–3.2	not sampled

^a Coordinates, depths and local time refer to the start (visual contact, 4–5 m from seabed) and end (start of probe recovery) of the survey.

^b Maximum distance considered in the horizontal “flyovers” is 4.9 m. Minimum distance corresponds to touch-downs.

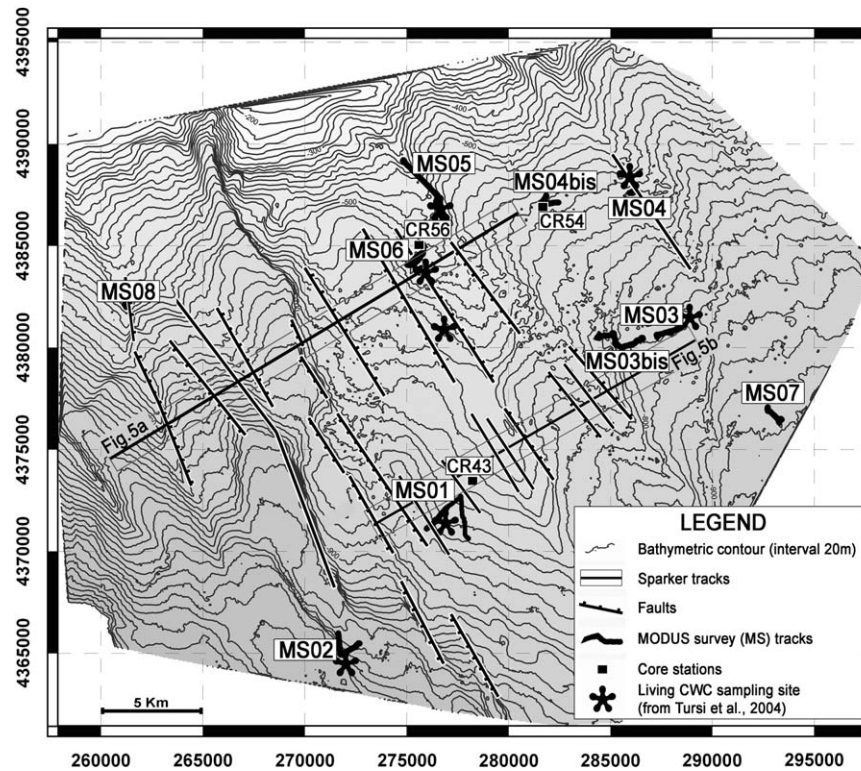


Fig. 4. Bathymetric chart (20-m contour interval) showing MODUS survey (MS) track lines and the main faults identified from the acquired geophysical data and from the literature (Auroux et al., 1985; Argnani et al., 2001) in the investigated area. Square indicates the core samples location and asterisks indicate the main sites in which living CWC were sampled before the beginning of the APLABES project (from Tursi et al., 2004). The insets locate the sparker profiles reported in the following figures (Fig. 5a and b) on which the faults have been identified.

seismic-stratigraphic data (Savini and Corselli, 2010). In particular, acoustic wipe-out zones (which in some cases can indicate gas accumulation within the sediments (Sager et al., 1999, and references therein) and peculiar seafloor hyperboles documenting changes in sediment roughness and/or porosity (as the presence of CWC can generate) were identified (Fig. 6). Based on these observations, the MODUS survey track lines were planned and performed.

2.2. Methane analysis in seawater

In total 31 seawater samples were collected at nine sites (Table 1 and Fig. 2). Replicate samples were taken from four bottles. Seawater was collected in 200 ml glass bottles sealed with silicon septa and aluminium caps. All samples were conditioned by adding 0.1% HgCl_2 to prevent bacterial consumption of CH_4 . Methane analyses were performed by head-space extraction (double syringe technique; Etiope, 1997; Rehder et al., 1998), in thermostatic conditions and GC-FID (Gas Chromatography-Flame Ionization Detector; Autofim II, Telegan, UK; detection limit 0.1 ppm, accuracy 4–5%). The reproducibility of replicate head-space samples was within $\pm 15\%$, as determined from 10 water samples in atmospheric equilibrium. Calibration was performed using atmospheric samples and Rivoira standards ($50 \text{ ppmv CH}_4 \pm 2\% \text{ in N}_2$).

2.3. Sediment sampling and analyses

During the CORSARO cruise (R/V Urania; April 2006), four samples of seafloor sediment were collected by a gravity corer (Table 2 and Fig. 2) at depths between 499 and 915 m. Sediment samples were placed into metal cans following standard

procedures (e.g., Orange et al., 2005). The head-space gas in the cans was analysed for light hydrocarbons ($\text{C}_1\text{--C}_6$), He, H_2 , Ar, O_2 , CO_2 , N_2 , CO, H_2S by gas chromatography (Carle AGC 100–400 with thermal-conductivity (TCD) and flame-ionization (FID) detectors; detection limit: CO_2 , N_2 , Ar, O_2 : 40 ppmv; H_2S : 150 ppmv; He and hydrocarbons: 10 ppmv; accuracy 2%; 10% at the detection limit) at Isotech Labs Inc. (Illinois, USA).

3. Results and discussion

Ten surveys from 380 to 1100 m.b.s.l. were completed within one week at eight selected sites (Fig. 4), getting more than 26 h of continuous video and instrumental recording.

The video images were carefully examined to assess abundance and distribution of the coral banks and their relationships with the morphological and geological structures (as discussed by Rosso et al., 2010; Savini and Corselli, 2010; Vertino et al., 2010). During the flyovers, the sonar of MODUS was able to detect even small blocks ($< 1 \text{ m}$ size) of corals, from distances above 50 m throughout a 120° horizon, anticipating their presence successively displayed by the video monitors (Fig. 7). This allowed to change the navigation direction following the sonar targets and to find even small coral patches, apparently isolated from larger mounds. The images do not show, however, any indication of gas seepage, such as bubbles, small craters, pockmarks or white bacterial mats.

Table 1 summarises the main parameters of the 10 surveys. In the last survey (MS8) only video images were recorded due to a temporary failure in the telemetry system. The probe “flyover” was on a distance from the seabed generally ranging from 1 to 3 m.

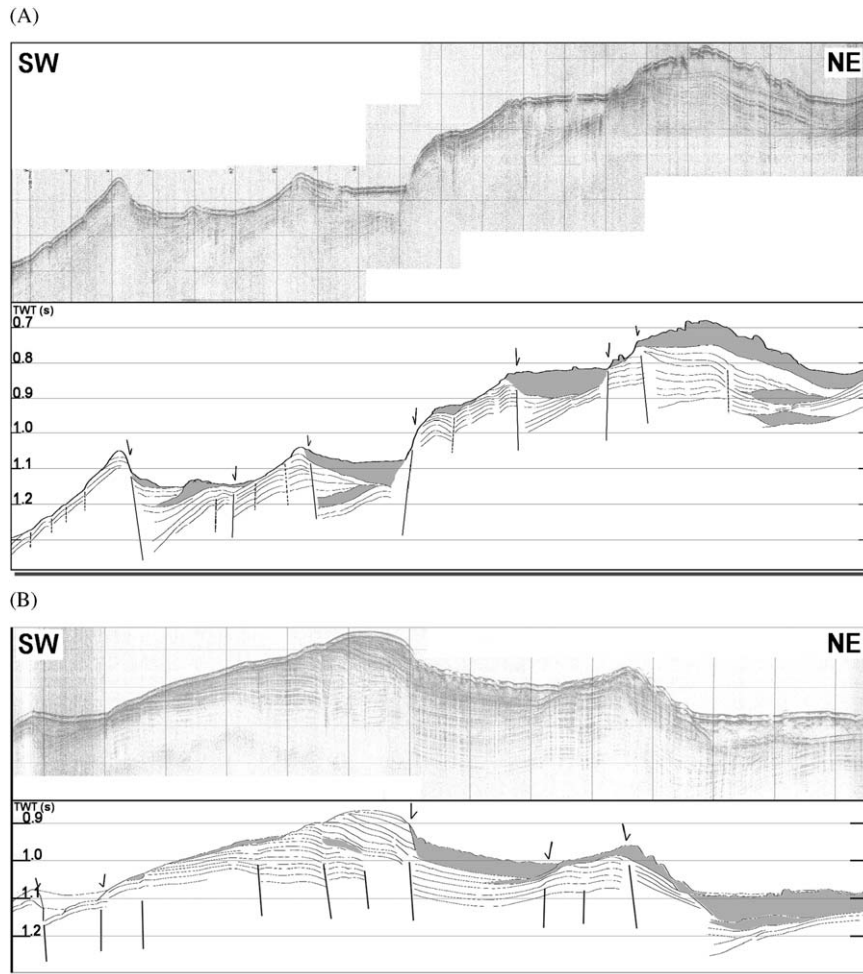


Fig. 5. Sparker profiles acquired during the CORSARO cruise (see Figs. 2 and 4 for locations) and their preliminary interpretation showing the main identified normal faults in the SML coral province. Grey areas indicate mass transport deposits.

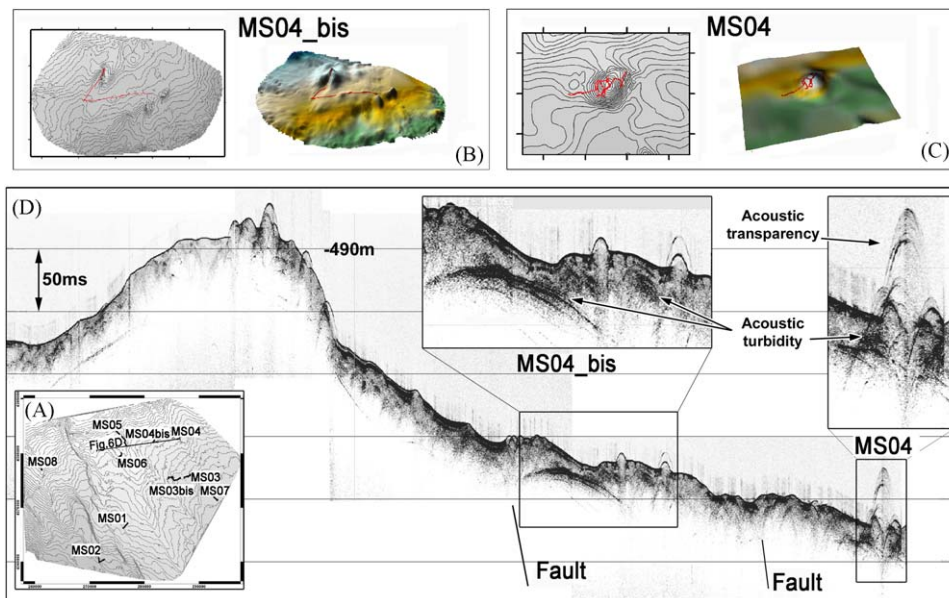


Fig. 6. Geophysical data from two sites investigated by the GAS-SCIPACK/MODUS (MS04 and MS04bis, see also Fig. 4 for locations). A: Map of the investigated area with location of the MODUS survey track lines and the high-resolution seismic profile here presented. B: MS04bis site contour map (2-m contour interval) and 3D-view from multibeam bathymetry. C: MS04 site contour map (2-m contour interval) and 3D-view from multibeam bathymetry. D: High-resolution seismic profile crossing the investigated sites, the highlighted insets show the amplitude anomalies identified from the data.

Table 2
Sediment sampling sites and wet versus dry sediment weights.

Station	CR 28	CR 43	CR 54	CR56
Site coordinates	39°50'55" N 17°38'00" E	39°28'59" N 18°25'07" E	39°36'17" N 18°27'21" E	39°34'57" N 18°23'22" E
Depth (m)	915	703	626	499
Weight dry (g) (only sediment)	555	510	480	498
Weight wet (g) (sediment+water)	900	910	895	890

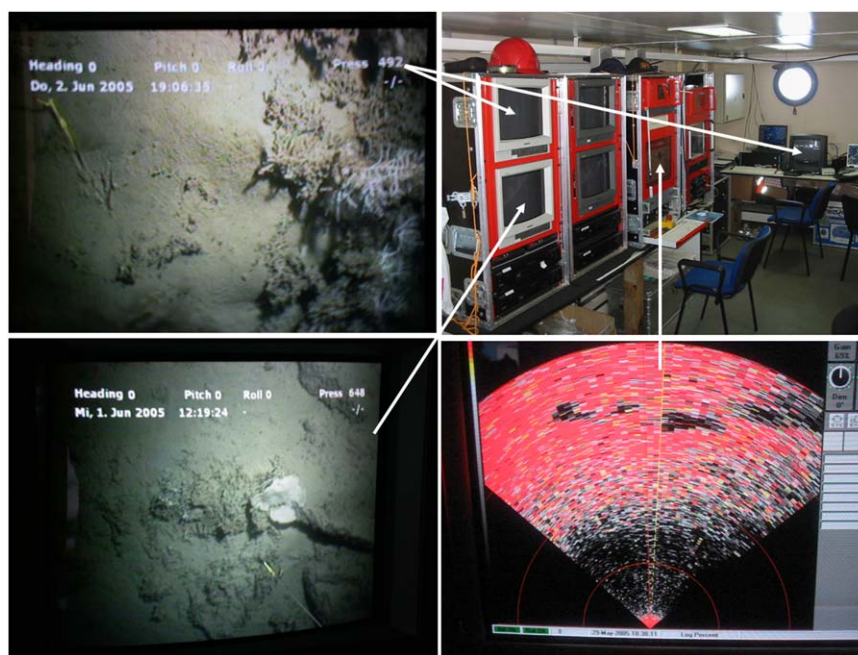


Fig. 7. Video and sonar images from the GAS-SCIPACK/MODUS system and its control room (top-right).

The data acquired by GAS-SCIPACK have been examined by cross-checking all recorded parameters. Plotting pressure, distance from the seabed, CTD and methane sensor data vs. a time axis gives an overall picture of the navigation and instrumental surveys. Summing pressure (corrected as depth) to the distance of the probe to the seafloor gives an indication of the seafloor depth during the “flyover”. The Niskin bottles were opened in each site close to seabed (distance < 1.5 m), close to coral colonies and sharp morphological changes, such as scarps.

Fig. 8 shows two examples of plot derivable from the GAS-SCIPACK data. These data can be compared with the position (coordinates) of the ship (roughly corresponding to the probe position ± 10 –15 m) recorded by GPS navigation system and with the video images. So, significant features visually observed (e.g., occurrence of corals, scarps, etc.), and related coordinates, can be marked in the GAS-SCIPACK data plot.

The methane signals have never showed variations above 0.05 V, implying that methane anomalies (respect to a background of about 2–4 nmol/l) likely did not exceed 25–75 nmol/l.

Voltage drops in the order of 0.01–0.04 V however, were recorded in several points in MS3, 4 and 6. All these drops appear to occur only in correspondence with physiographic lows, at the base of mound slopes, when the probe was very close to the seabed (< 1.7 m) or after touch-down, with remobilization of the sediments. Touch-downs on the top of the mounds did not show significant voltage changes.

Table 1 lists the main descriptive statistics (minimum, maximum, average) of the GAS-SCIPACK data-set and the methane concentration from the GC-FID analyses on the seawater samples.

The GC analyses of seawater collected by the Niskin bottles showed methane concentrations close to the typical background value (ASW, Air Saturated Water: about 2–4 nmol/L); values above 10 nmol/L were detected only at sites MS4 and MS4bis, in correspondence with a morphological scarp (Fig. 8).

The sediment analyses (Table 3) did not show any hydrocarbon anomaly. Methane and alkane concentration in the can head space were below the detection limit of 10 ppmv. However, the head-space gases showed anomalously high values of hydrogen, nitrogen in all samples and elevated helium concentrations in sample CR43. The N_2/O_2 ratios ranged from 20 to 166, which is much higher than the atmospheric ratio of ~ 4 and suggests that air contamination is minimal. If N_2 comes from air contamination then O_2 must have been metabolised. The N_2/Ar - and He/Ar - ratios for sample CR43 were about 80 and 0.0024, well above the dissolved air ratios of ~ 35 and 0.0002, respectively. The excess N_2 could derive from denitrification, since oxides of nitrogen comprise important components of the nitrogen cycle in coral ecosystems (Yakimov et al., 2006) and can be used *in lieu* of O_2 as terminal electron acceptors by denitrifying bacteria. Alternatively, N_2 could derive from a deep geologic source. This possibility would be supported by the high concentrations of hydrogen (39–480 ppmv) and helium (28 ppmv) at Site CR43, which are

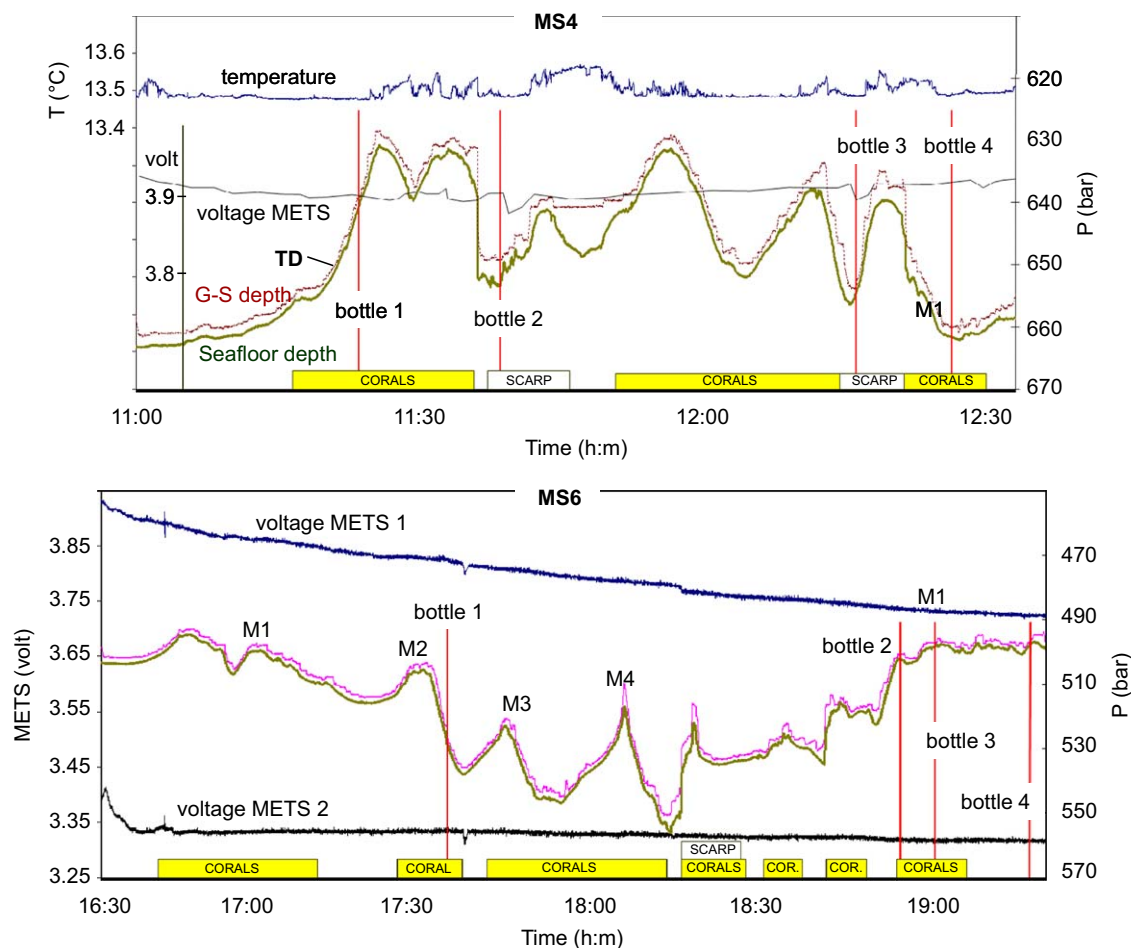


Fig. 8. Plots of GAS-SCIPACK recording during flyovers at mounds 4 and 6. Temperature (for MS4), voltage of methane sensors (METS), seafloor depth, GAS-SCIPACK depth and events of bottle sampling are shown. The bars along the x axis indicate the occurrence of corals or scarps as shown by video-cameras. TD: Touch-down. M1-M4 refer to four individual mounds recognised in the MS6 area.

Table 3

Compositional analyses of head-space gas in the sediment samples (% v/v).

Sample	Depth (m)	He	H ₂	Ar	O ₂	CO ₂	N ₂	CH ₄	C ₂ –C ₆
CR 28	915	bdl	0.0481	1.22	0.59	0.27	97.88	bdl	bdl
CR 43	703	0.0028	0.0039	1.17	4.98	0.20	93.64	bdl	bdl
CR 54	626	bdl	0.0282	1.21	3.60	0.23	94.93	bdl	bdl
CR 56	499	bdl	0.0524	1.19	3.19	0.23	95.34	bdl	bdl

Bdl: below detection limit (10 ppmv).

generally constituents of gas from deep crustal sources. However, any interpretation is premature; further data preferably of deeper samples and including the analysis of N isotopes, would help to decipher the origin (contamination, natural shallow or deep sources) of the gas anomalies.

4. Conclusions

The images allowed to assess the distribution, abundance and geometry of the coral colonies, most of which are developed over morphological rises, often characterised by tectonic scarps. No

significant occurrence of methane was detected either in seawater or in the underlying sediments. No bubbles or other direct seepage indications were observed. Methane concentrations in seawater were generally close to equilibrium with the atmospheric concentrations. Weak methane anomalies, recorded both by the semiconductor sensors as voltage variations and by the GC analyses, were on the order of a few tens of nmol/L. They occurred only at some physiographic lows, at the base of mound slopes or fault-linked scarps, when the probe was very close to the seabed (< 1.7 m) or after touch-down. But, touch-downs on the top of the mounds did not show significant voltage changes or methane-concentration anomalies. The sediment analyses also showed the

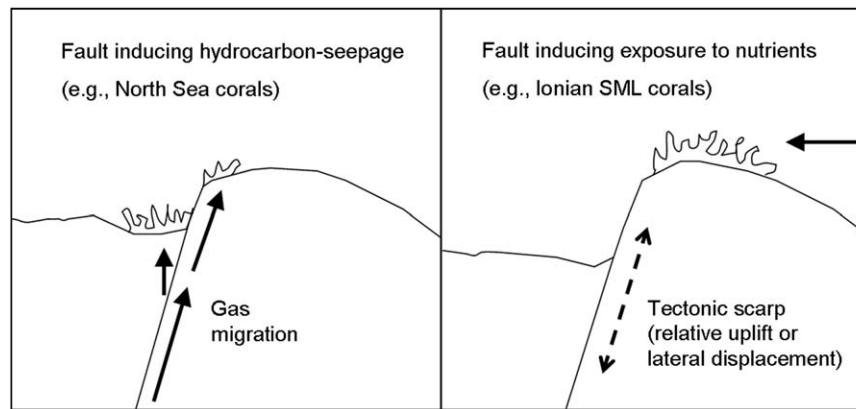


Fig. 9. Sketch model of fault-linked development of deep-water coral mounds. The arrows indicate nutrient-rich fluid: (a) hydrocarbon seepage (e.g., [Hovland, 2005](#)); (b) ocean currents.

lack of methane anomalies. It is possible that the weak anomalies simply reflect local bacterial production of CH_4 under more reducing conditions.

Anomalous concentrations of N_2 could be due to denitrification and/or gas migration from a deep source, as the high H_2 and He would suggest. The faults do not bear significant amounts of gaseous hydrocarbons, as previously suggested by geophysical images, but they might provide a pathway for some N_2 -rich crustal gases, like those associated to the hydrocarbon systems of the nearest Ionian seepage-zone off western Greece ([Etiope et al., 2006](#)). The faults seem to play a fundamental role in the coral-reef location: they determine a favourable physiographic exposure to nutrient-rich currents coming from the north-eastern sector of the basin ([Fig. 9](#)).

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