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Molecular and carbon isotopic variability of hydrocarbon gases from mud volcanoes in the Gulf of Cadiz, NE Atlantic

Alina Stadnitskaia [a,b,*], Michail K. Ivanov [b], Valentina Blinova [b], Rob Kreulen [d], Tjeerd C.E. van Weering [a,c]

[a] Royal Netherlands Institute for Sea Research (NIOZ), P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands
[b] Geological Faculty, UNESCO-MSU Centre for Marine Geosciences, Moscow State University, Vorobjevy Gory, Moscow 119899, Russian Federation
[c] Department of Paleoclimatology and Geomorphology, Free University of Amsterdam, de Boelelaan 1085, 1081 HV Amsterdam, The Netherlands
[d] ISOLAB, 1e Tieflaarsestraat 23, 4182 PC Neerijnen, The Netherlands

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Abstract

Investigations of molecular and carbon isotopic variability of hydrocarbon gases from methane through butanes (pentanes) have been performed on six mud volcanoes from two fluid venting provinces located in the Gulf of Cadiz, NE Atlantic. The main aims were to define the basic gas types, to describe their geochemical characteristics in relationship to their sources, and to determine the secondary effects due to migration/mixing and microbial alteration. Hydrocarbon gas data reveal two groups of gases. Despite the different maturation characteristics, both gas groups are allochthonous to the erupted mud breccia and represent a complex of redeposited, secondary migrated, mixed, and microbially altered hydrocarbons. It may possibly imply the presence of hydrocarbon accumulations in the deep subsurface of the Gulf of Cadiz.

Keywords: Hydrocarbon gas; Mud volcanoes; The Gulf of Cadiz

1. Introduction

In the various manifestations of seeps on and beneath the seafloor, migrated hydrocarbon-rich fluids exert a distinct influence on the biological resources and chemistry of ocean, geology, and environment, consequently linking the lithosphere, biosphere, hydrosphere, and atmosphere. Mud volcanoes (MVs) are representative seepage-related geomorphological features and the most imposing indication of fluid venting (Ivanov et al., 1998). In general, MVs and seeps are direct indicators of hydrocarbon migration providing sign of hydrocarbon potential in the deep sediments (Guliev and Feizullayev, 1997; Ivanov et al., 1998). The connection between seepages and deep-sited hydrocarbon reservoirs has been advocated by Link (1952) who stated that ‘oil and gas seeps gave the first clues to most oil-producing regions. Many great oil fields are the direct result of seepage drilling’. MVs commonly occur in petroliferous regions (Guliev and Feizullayev, 1997). They are expressed in the sea floor relief either as mounds or as negative collapse structures, caused by catastrophic eruption of fluids, especially hydrocarbon gases (predominantly methane), hydrogen sulfide, carbon dioxide, and petroleum products (Ivanov et al., 1998).

A region of active mud volcanism and gas venting was recently discovered within the Gulf of Cadiz, NE Atlantic (Kenyon et al., 2000; Gardner, 2001; Pinheiro et al., 2003). Previous multidisciplinary investigations in this area, both industrial and scientific, showed a widespread occurrence of hydrocarbon-enriched fluid discharge on the sea floor (Baraza and Ercilla, 1996; Baraza et al., 1999; Ivanov et al., 2000, 2001; Somoza et al., 1999, 2002; Gardner, 2001; Kenyon et al., 2001; Mazurenko et al., 2002, 2003; Pinheiro et al., 2003). Active mud volcanism and associated gas hydrates were for the first time documented in the deep part of the Gulf of Cadiz (from 900 to over 3000 m of the water depth) during Training Through Research (TTR) cruises of R/V Professor Logachev which were carried out within the framework of the UNESCO-IOC ‘Floating University’ Programme (Kenyon et al., 2000).

On the basis of side-scan sonar mosaic and multibeam bathymetry mapping (SEAMAP) by the Marine Physics Branch of the Naval Research Laboratory (USA) in

* Corresponding author. Address: Royal Netherlands Institute for Sea Research (NIOZ), P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands. Tel.: +31 222 369 566; fax: +31 222 319 674.
E-mail address: alina@nioz.nl (A. Stadnitskaia).

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cooperation with the Hawaii Mapping Research Group (HMRG) and the Naval Oceanographic Office (NAVOCEANO) in 1992, detailed geophysical and geological surveys during TTR-9 (1999) cruise led to the discovery of a new mud volcano province along the Moroccan–Spanish continental margin, Western Moroccan field (WMF; Fig. 1) (Kenyon et al., 2000; Ivanov et al., 2000; Gardner, 2001). A follow-up study in the Gulf of Cadiz, cruise TTR-10 (2000), discovered an additional mud volcano province on the deep South Portuguese continental margin, i.e. the deep South Portuguese field (DSPF; Fig. 1) (Kenyon et al., 2001; Ivanov et al., 2001; Pinheiro et al., 2003).

Until now, detailed investigations of molecular and isotopic characteristics of hydrocarbon gas and organic matter in mud volcanoes (MVs) of the Gulf of Cadiz have not been carried out. Here, we report the results on molecular and carbon isotopic characteristics of hydrocarbon gas collected in gas saturated pelagic sediments and mud volcano deposits (mud breccia) from six MVs in the Gulf of Cadiz (Fig. 2). The current investigation concentrated upon two primary objectives. One of the objectives was to determine the presence of thermogenic hydrocarbons that migrated from the deep subsurface. In addition, it was projected to deduce whether hydrocarbon gases are indigenous to the erupted mud volcano sediments, so called mud breccias, or not. The second major objective of this study is to identify microbial alteration processes related to the presence of hydrocarbon gas, primarily methane, in already erupted mud volcano sediments and in the shallow subsurface. A particular effort was directed towards determination of the content, concentration levels, and correlation between individual hydrocarbons and total organic carbon (TOC) content in the sediments. Hydrocarbon gases have been characterized to their types/maturity, possible sources, and to their alteration due to microbial actions using molecular and stable carbon isotope compositions of C_1–C_4 alkanes.

2. Geological background

The Gulf of Cadiz is located in the Southwestern part of the Iberian margin (in the Northeastern Atlantic Ocean), West of Gibraltar Strait. It is positioned on the transition area between the Gloria transform fault zone delineating the African–Eurasian plate boundary in the Atlantic and the Western-most part of the Alpine–Mediterranean orogenic belt (Maldonado et al., 1999; Somoza et al., 2002; Medialdea et al., 2004).

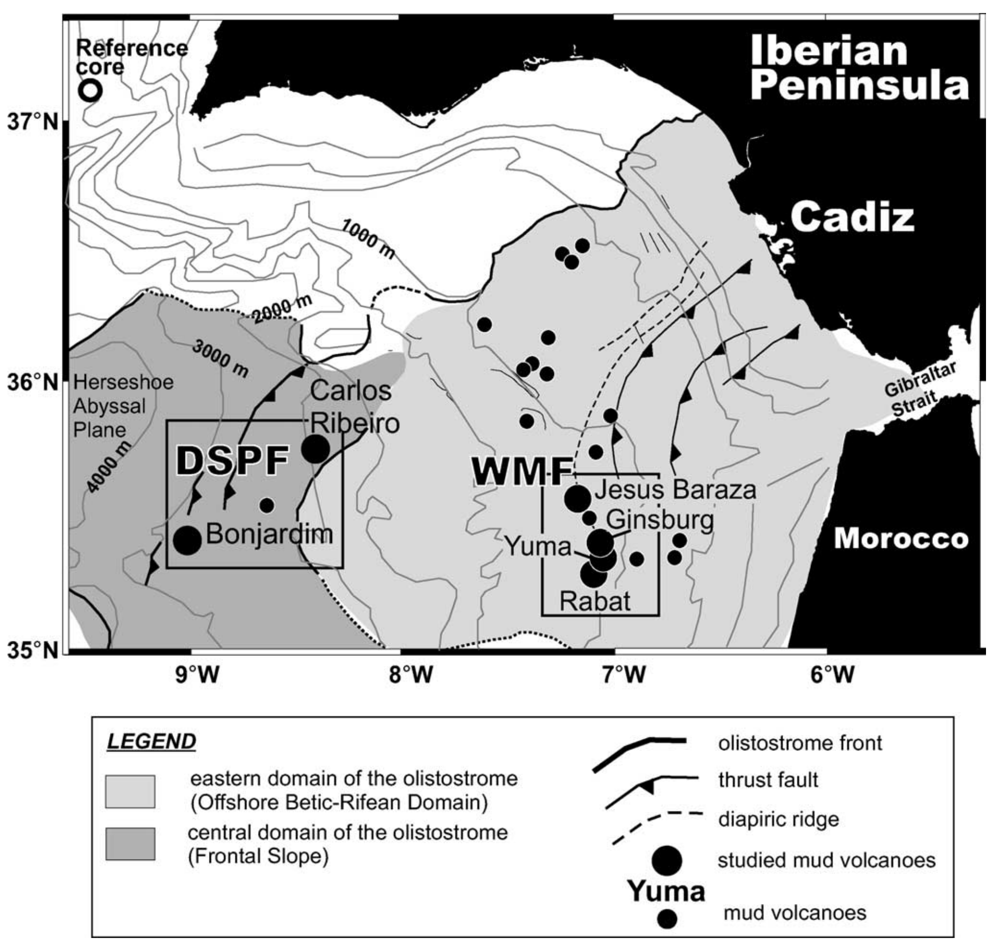

Fig. 1. Geological map, simplified bathymetry of the Gulf of Cadiz, and the location of studied mud volcanoes (compilation of TTR data 1999–2001 and Medialdea et al., 2004). The boundary of the olistostrome body and names of its structural domains, location of thrusts and diapiric ridges are after Medialdea et al. (2004). DSPF indicates the deep South Portugese field; WMF is the Western Moroccan field.

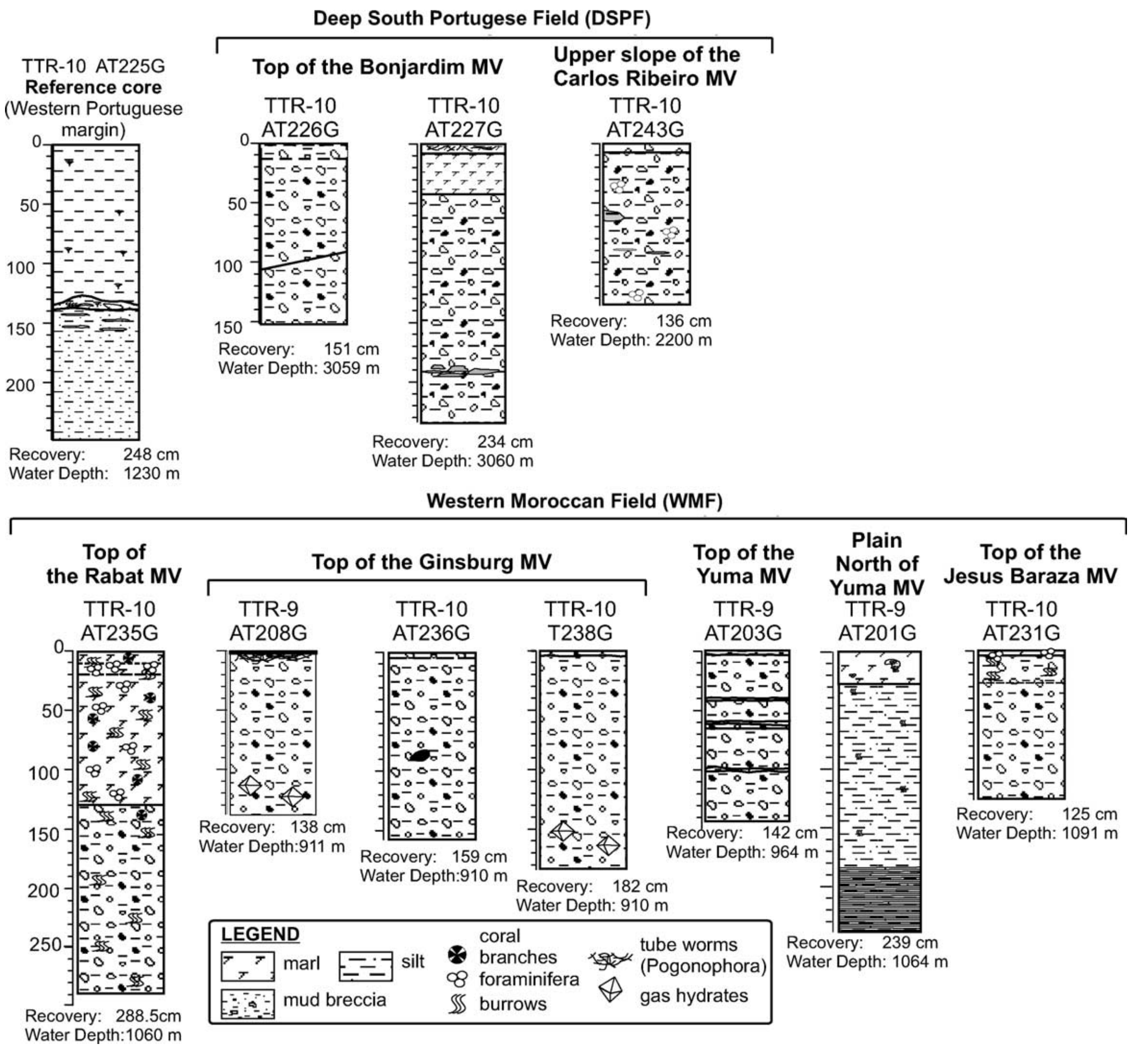

Fig. 2. Schematic lithology of the studied cores.

The geological evolution of the area is very complex, entailing several phases of rifting, convergence, and strike-slip motions since the Triassic (Srivastava et al., 1990; Maldonado et al., 1999; Maldonado and Nelson, 1999). At present, the tectonic regime of the Gulf of Cadiz is characterized by moderate tectonic subsidence and local transpressive tectonics (Maldonado et al., 1999).

A particular structure in the area is the large olistostrome, extending through the Gulf in a Southwest direction (Maldonado et al., 1999; Fig. 1). The main emplacement of the olistostrome close to its present location took place during the late Tortonian as a consequence of a rapid increase of basement subsidence rates (Maldonado et al., 1999). The mud volcano provinces discovered and documented during the TTR-9 and TTR-10 cruises, are located 'within' the olistostrome body (Fig. 1). The WMF (Gardner, 2001; Kenyon et al., 2000; Pinheiro et al., 2003) includes the Rabat, Ginsburg, Yuma, and the Jesus Baraza MVs. These structures are grouped in the Eastern domain of the olistostrome body, indicated by Medialdea et al. (2004) as offshore Betic-Rifean domain (Fig. 1). The presence of the MVs appears to be related to fault systems (Gardner, 2001; Pinheiro et al., 2003) and to diapirs forming a set of parallel ridges with a NE–SW trend (Medialdea et al., 2004). The Bonjardim and the Carlos Ribeiro MVs are the deepest-located structures within the DSPF (Fig. 1). These MVs occur in the central domain of the olistostrome, the frontal slope of the Allochthonous wedge area (Medialdea et al., 2004; Fig. 1).

3. Materials and methods

Seismic recording by air gun, profiling by long range OCEAN, and high-resolution deep towed OREtech side-scan sonar systems, led to recognition of a considerable number of MVs within the WMF and DSPF (Kenyon et al., 2000, 2001). Six of these MVs Rabat, Ginsburg, Yuma, Jesus Baraza (WMF), and Bonjardim and Carlos Ribeiro (DSPF), were selected for sampling and subsequent detailed geochemical analyzes (Fig. 1). The location of each core site is given in Table 1.

All cores, collected during the TTR-9 and TTR-10 cruises, were obtained using a 6 m long gravity corer (ca. 1500 kg) with an internal diameter of 14.7 cm (Kenyon et al., 2000, 2001). Subsampling for hydrocarbon gas analysis was performed

Table 1
General information on the studied cores from the Gulf of Cadiz (Kenyon et al., 2000, 2001)

Core No.	Latitude	Longitude	Geographical setting	Depth (m)	Recovery (cm)	Remarks
Reference core						
TTR10 AT225G	37°06.002′N	09°28.051′W	Portuguese margin, the Marques de Pombal area	990	248	Hemipelagic sediments
Western Moroccan field						
TTR9 AT201G	35°27.305′N	07°06.518′W	Plain to the North of the Yuma MV	1064	239	Pelagic sediments
TTR9 AT203G	35°25.391′N	07°06.026′W	Crater of the Yuma MV	964	142	Mud breccia, gas saturated, strong sulfide smell
TTR9 AT208G	35°22.392′N	07°05.321′W	Crater of the Ginsburg MV	911	138	Mud breccia, gas saturated, strong sulfide smell, gas hydrtaes
TTR10 AT236G[a]	35°22.409′N	07°05.328′W	Crater of the Ginsburg MV	910	159	Mud breccia, gas saturated, strong sulfide smell
TTR10 AT238G[a]	35°22.409′N	07°05.330′W	Crater of the Ginsburg MV	910	182	Mud breccia, gas saturated, strong sulfide smell, gas hydrtaes
TTR10 AT231G[a]	35°35.452′N	07°12.048′W	Top of the Jesus Baraza MV	1091	125	Mud breccia, gas saturated, strong sulfide smell, 4 cm of pelagic sediments with Pogonophora tube worms
TTR10 AT235G	35°18.858′N	07°07.997′W	Top of the Rabat MV	1060	288	The upper ca.130 cm is pelagic sediments, the rest is mud breccia
Deep South Portuguese field						
TTR10 AT226G[a]	35°27.603′N	09°00.023′W	Top of the Bonjardim MV	3059	151	Mud breccia, gas saturated, strong sulfide smell. Gas hydrates were recovered from the structure
TTR10 AT227G[a]	35°27.851′N	09°00.028′W	Terrace below the top of the Bonjardim MV	3060	234	The top ca. 42 cm is pelagic sediments with Pogonophora tube worms. The rest is mud breccia, gas saturated, strong sulfide smell
TTR10 AT243G[a]	35°47.217′N	08°25.313′W	Top of the Carlos Ribeiro MV	2200	136	Mud breccia, gas saturated, strong sulfide smell

[a] Cores chosen for stable carbon isotope study.

taking into consideration the lithology of the recovered sediments. The standard sub-sampling and degassing procedures of sampled sediments, followed by chromatographic analysis was done. The degassing was accomplished according to the head-space technique (Bolshakov and Egorov, 1987). To reduce intensive degassing, especially from mud breccias with gas hydrates, the subsampling of such sediments was carried out in a cold-room with a constant temperature of ca. −20 °C.

The molecular composition of the C_1 to C_5 hydrocarbons including alkenes (ethene, propene and butene) and alkanes with isomeric molecular structure (iC_4 and iC_5) were determined in the laboratory using a gas chromatograph (GC) equipped with an on-column injector and a flame ionization detector. Gas components were separated on a 3 m packed column with activated Al_2O_3 as a stationary phase. The samples were injected at 40 °C and this temperature was held for 10 min. Then the GC oven temperature was subsequently raised to 70 °C at a rate of 1 °C/min. The temperature was then held constant for 20 min. The results presented here are calculated according to the volume of wet sediment. It is worth to note that in spite of the absolute notations for hydrocarbon gases, part of the gases were lost on deck due to active degassing of the recovered sediments during sectioning and cutting of the cores. Besides, it is well known that the 'head-space' technique is a qualitative rather then a quantitative method. In order to indicate the trend of the methane distribution profiles and to indicate a rough level of gas saturation even with its partial loss, we decided to present hydrocarbon gas data in absolute (i.e. ml/l of wet sediment) values.

The carbon isotope ratios from C_1 to C_4 including iC_4 hydrocarbon gases were measured on a Finnigan Delta S mass spectrometer with a HP 5890 GC and a GC-combustion interface. Methane was separated on a 5 Å molecular sieve plot column using either split- or split-less injection, depending on the concentrations. Alkanes C_2–C_4 were cryogenically enriched (trapping in liquid nitrogen) and separated on a poraplot-Q column. The carbon stable isotope concentrations are reported in the δ-notation (‰) relative to Vienna Pee Dee Belemnite (VPDB) standard. The overall precision for stable carbon isotope measurements by parallel definitions was ca. 0.3‰ for C_1 and C_{2+}.

The determination of the total organic carbon (TOC) content was carried out on samples from the same intervals as used for the hydrocarbon gas analysis. After decalcification of the samples, the measurements were accomplished on a Fisons Instruments NCS-1500 Elemental Analyzer using flash combustion at 1013 °C. Standard deviations of duplicate measurements were ca. 0.3%.

4. Results

4.1. Sediments

A great variety of sediment types, from both MVs and surrounded areas, were recovered and described during the TTR-9 and TTR-10 cruises in the Gulf of Cadiz (Kenyon et al., 2000, 2001; Pinheiro et al., 2003). These reflect different initial depositional environments, MV activity and complex hydrologic conditions among the two MV provinces. Sediments from all studied MVs showed clear indications of gas saturation. This was manifested by extensive degassing, a strong smell of sulfide and the presence of chemosynthetic fauna such as diverse Pogonophora tube worms.

The characteristic feature of the mud breccias from the Ginsburg, the Yuma, and the Bonjardim MVs is the presence of very thin cover of pelagic sediments which indicates that the sampling sites were located on a relatively recent mud flows (Fig. 2). Methane-related Pogonophora tube worms were found at the surface layers of the Ginsburg (TTR9 AT208G) and the Bonjardim (TTR10 AT227G) MVs and gas hydrates were observed below 1 m sediment depth at the Ginsburg MV (TTR9 AT208G and TTR10 AT238G) (Kenyon et al., 2000, 2001; Gardner, 2001; Pinheiro et al., 2003).

A reference core, TTR-10 AT225G, was taken in the Western Portuguese margin. The core consisted of olive-gray clayey hemipelagic sediments, mainly homogenous and structureless, occasionally bioturbated, with silty admixture and some foraminifera (Table 1, Fig. 2).

4.2. Molecular composition of hydrocarbon gas

4.2.1. Reference core

Hemipelagic sediments of core TTR10 AT225G, show methane concentrations several orders of magnitude higher than considered for background methane levels in near-surface sediments (ca. 20–50 ppb; cf. Whiticar, 1994). Unsaturated hydrocarbons, ethene ($C_{2:1}$) and propene ($C_{3:1}$), are generally more abundant than saturated hydrocarbons, ethane (C_2) and propane (C_3), which is indicative for recent diagenetic microbial activity (Hunt, 1975; Whiticar et al., 1985; Whiticar, 1994).

Fig. 3A shows that TOC and hydrocarbons are not completely related. The presence of tracks of bioturbation in the uppermost 135 cm and numerous small lenses of silt/sand in a clayey matrix can influence both the distribution and the activity of microorganisms and, as a consequence, hydrocarbon

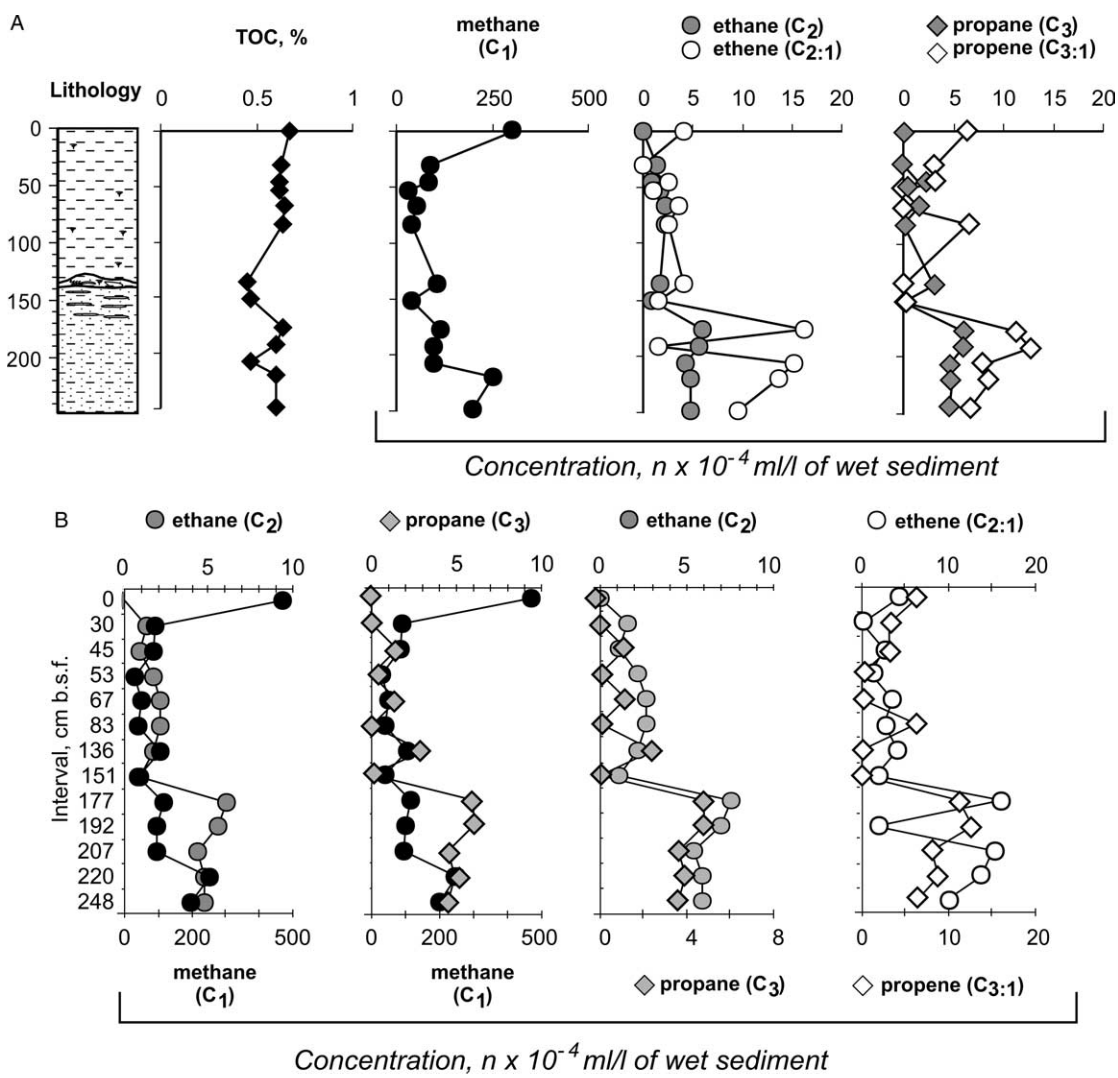

Fig. 3. Distribution of hydrocarbon gas along sediments of reference core TTR10 AT-225G. (A) TOC, C_1–C_3 hydrocarbon gas profiles; (B) two-scale plots showing the relationship between C_1, C_2, C_3, $C_{2:1}$, and $C_{3:1}$.

gas profiles. It is unlikely that sediments from the reference core contain petroleum-derived components. This is indicated by the predominance of $C_{2:1}$ and $C_{3:1}$, which can be formed by marine organisms and normally is nearly absent in thermogenic gases (Hunt, 1979). Simultaneously, the reference core shows a good correlation between C_1 and C_3 gas components (Fig. 3B). All together imply the in situ development of hydrocarbon gas due to microbial organic matter degradation.

4.2.2. Sediments from MVs

A majority of the sediments from the MVs of the Gulf of Cadiz is characterized by high methane concentrations relative to the reference core. Methane is the dominant hydrocarbon in all samples, comprising from 66 to 99% of the total hydrocarbon gas. The lowest methane content is mainly observed in the uppermost intervals. On average, methane from the WMF and DSPF composes 97 and 92%, respectively, indicating relatively dry characteristics of the gas in both areas.

The wet gas components (C_{2+}) exhibit a different molecular composition and concentration levels in the WMF and in the DSPF provinces. With exception of the sediments collected from the plain to the North of the Yuma MV (TTR9 AT201G) and from the crater of the Rabat MV (TTR10 AT235G), five saturated aliphatic compounds, ethane (C_2), propane (C_3), *iso*-butane (iC_4), *normal*-butane (nC_4), *iso*-pentane (iC_5), and *normal*-pentane (nC_5) have been identified in the majority of samples. Ethane is the dominant hydrocarbon among the methane homologues, with a highest concentration of 4 ml/l. The maximum concentration of propane is 1.0 ml/l. Butanes (iC_4 and nC_4) sometimes exceed the level of propane. Since higher hydrocarbons (C_5–C_7) can be significantly fractionated due to condensation effects at surface pressure–temperature conditions, a selection of the data on iC_5 and nC_5 hydrocarbons is presented.

4.2.2.1. Western Moroccan field (WMF). Methane. Sediments collected from the craters of the Ginsburg (TTR9 AT208G, TTR10 AT236G, and TTR10 AT238G) and the Yuma (TTR9 AT203G) MVs show the highest methane concentrations so far measured in the Gulf of Cadiz, 292 and 207 ml/l, respectively (Fig. 4). These values signify an ample evidence of methane migration or generation. In contrast, methane concentrations in pelagic sediments collected from the plain to the North of the Yuma MV (TTR9 AT201G) are considerably lower relative to the mud breccia from the crater (from 113.0×10^{-4} to 3.7 ml/l). Such a difference in methane levels between the crater and plain areas indicates that active venting is principally concentrated within the central part of the Yuma MV.

Sediments from the crests of the Rabat (TTR10 AT235G) and the Jesus Baraza (TTR10 AT231G) MVs (Fig. 1) also demonstrate discernable methane levels. The methane concentrations, however, are to a great extent lower compared with those in the mud breccias from craters of the Ginsburg and the Yuma MVs (Fig. 4). Hence, the methane concentration data indicate that the Ginsburg and the Yuma are the most active MVs among the four investigated within the WMF, and that the present fluid flow is mainly found in these structures.

Other light hydrocarbons (C_{2+}). The anomalies of C_{2+} levels, as well as for the C_1, are related to mud breccias from the main craters of the Ginsburg (sampling sites TTR10 AT236G, TTR10 AT 238G) and the Yuma (TTR9 AT203G) MVs (Fig. 5). Gas measurements show that the concentration levels of ethane through pentanes (C_2–C_5) in these structures are the highest ever detected in the Gulf of Cadiz. At $\sim$50 cm below sea floor (bsf), the mud breccias contain 2–3 orders of magnitude more of each of the hydrocarbon gases than the reference core (Fig. 3a). There is no correlation between hydrocarbon gases and TOC content, indicating the allochthonous nature of C_{2+} alkanes to the mud breccias.

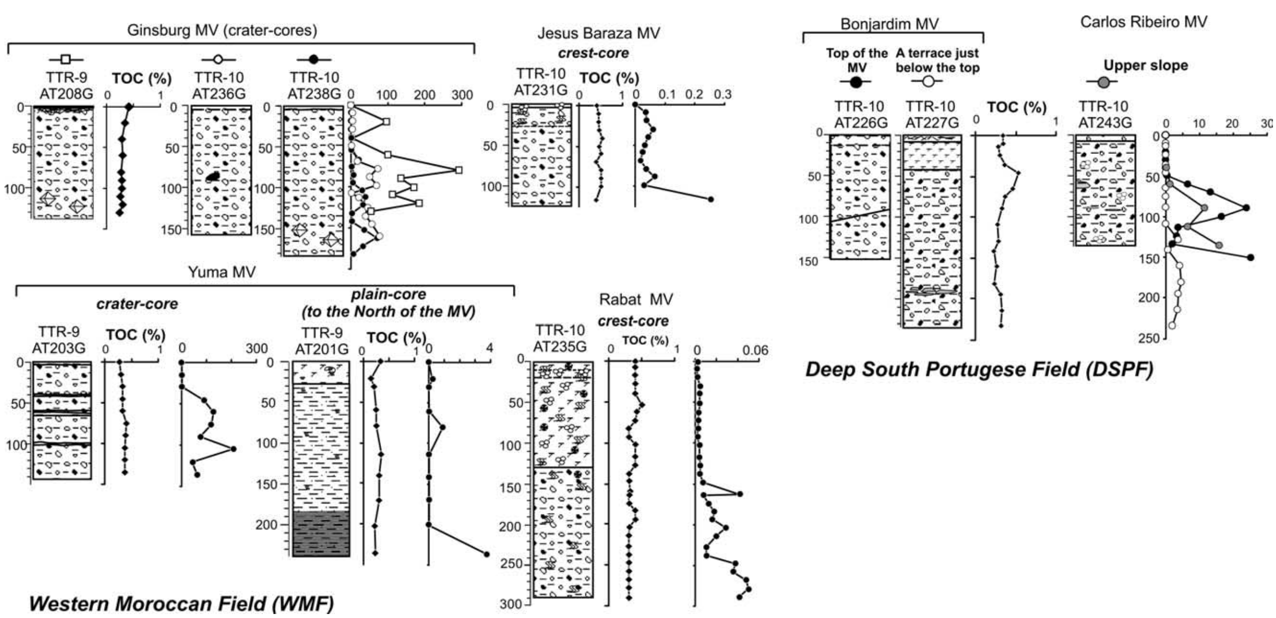

Fig. 4. Methane concentrations (ml/l of wet sediments) and TOC (%) versus depth in mud volcano sediments from the Western Moroccan field (WMF) and from the deep South Portuguese field (DSPF). For core lithologies see Fig. 2.

The plain-core from the Yuma MV (TTR9 AT201G) and the crater-core from the Rabat MV (TTR10 AT235G) are characterized by presence of only C_2 and C_3 hydrocarbons with concentration levels close to the background values. Mud breccia from the Rabat MV is overlaid by ca. 130 cm of pelagic sediments, indicating relatively old mud flow and lack of fluid transport processes. Even though, sediments from both sampling locations show absence of correlation between TOC and hydrocarbon gas distributions. This denotes an allochthonous nature of the gaseous components.

4.2.2.2. Deep South Portuguese field (DSPF). Methane. The deep-seated Bonjardim (sampling sites TTR10 AT226G, TTR10 AT227G) and Carlos Ribeiro (TTR10 AT243G) MVs

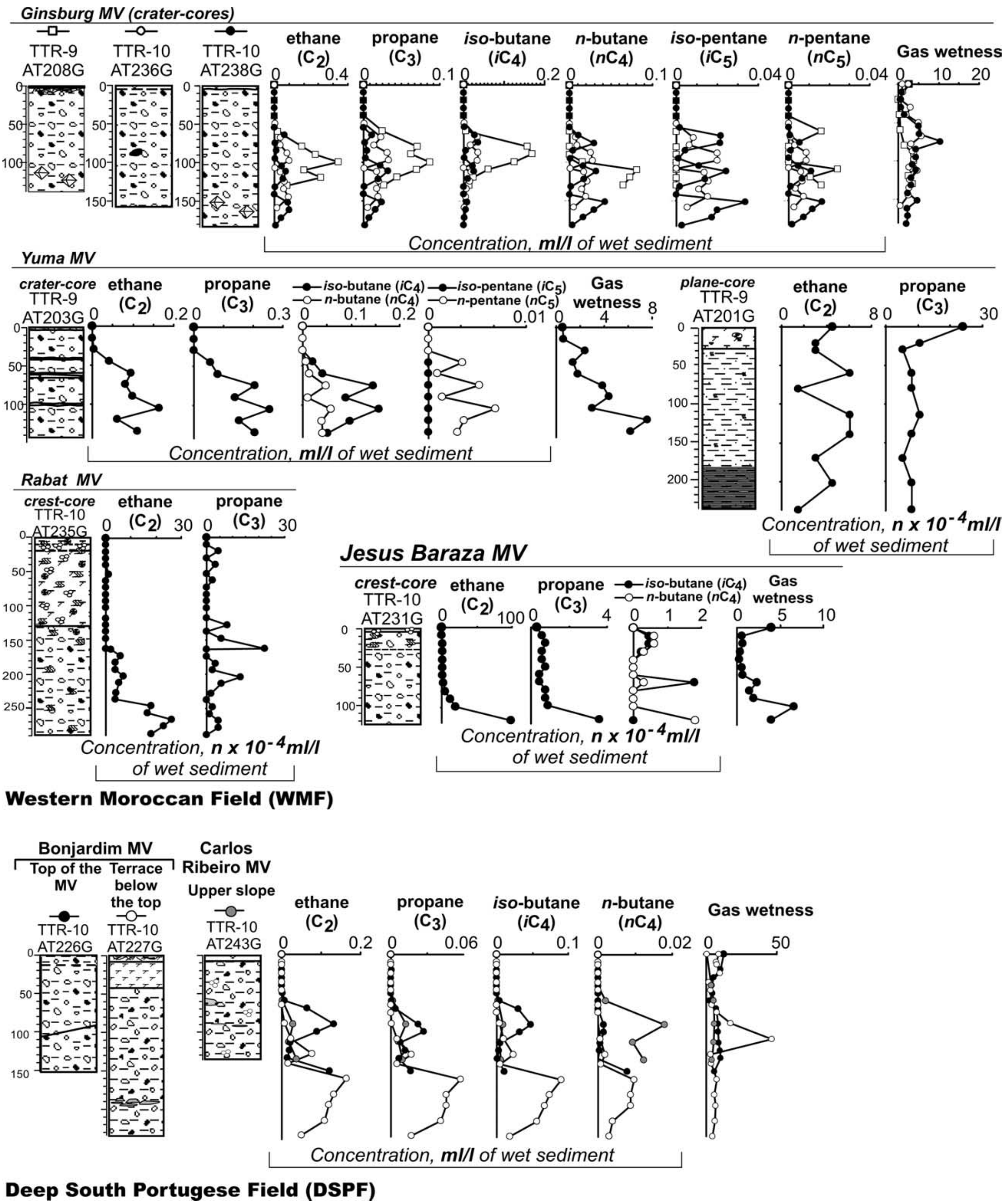

Fig. 5. C_{2+} concentrations versus depth in mud volcano sediments from the WMF and DSPF. For the core lithologies see Fig. 2.

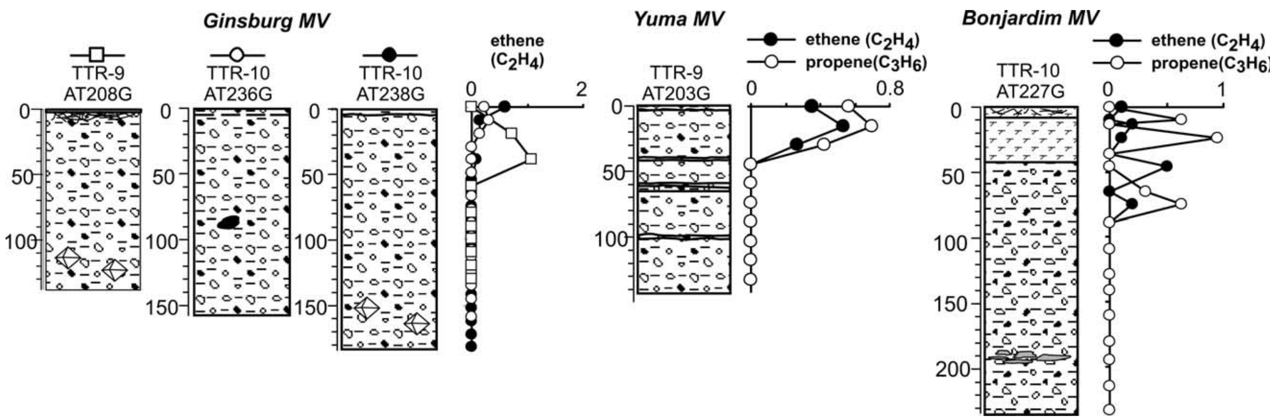

Fig. 6. Examples of alkene occurrences. Concentrations $n \times 10^{-4}$ ml/l of wet sediment. Alkenes occur in relation with the 'methane's consumption-signature' and C_{2+} diminution. This suggests that the formation of unsaturated hydrocarbons is related to the consumption of C_{2+}. For the core lithologies see Fig. 2.

(Fig. 1) show methane concentrations from 0.1 to 25 ml/l which are considerably higher relative to the measured background values. Compared with the methane concentrations from the cores of the Ginsburg and the Yuma MVs crater (WMF), the methane level in the Bonjardim and the Carlos Ribeiro MVs is lower (Fig. 4).

Other light hydrocarbons (C_{2+}). The C_{2+} levels in the Bonjardim (TTR10 AT 226G, TTR10 AT 227G) and the Carlos Ribeiro (TTR10 AT 243G) MVs, are similar to those determined in the craters of the Yuma and the Ginsburg MVs (WMF). High concentrations of butanes (iC_4 and nC_4) and pentanes (iC_5 and nC_5) were detected in all sampling locations within the DSPF (Fig. 5). None of the distribution profiles show a relationship with the TOC content, implying that C_{2+} alkanes are not indigenous to the erupted mud breccias.

Unsaturated hydrocarbon gases in WMF and DSPF. Appearance of unsaturated gases, ethene ($C_{2:1}$) and propene ($C_{3:1}$), is coherent with C_{2+} diminutions. Such a tendency is noticed for the sediments from the crater/crest of the Yuma, Ginsburg, Jesus Baraza, and the Bonjardim MVs (Figs. 5 and 6). It is not clear which peculiar microorganisms and via which pathways are capable to degrade wet gas components and, directly or indirectly, biosynthesize unsaturated hydrocarbon gases. Nonetheless, the occurrence of the alkenes in relation with the 'methane's consumption-signature' and C_{2+} diminution, additionally may suggests that wet gas components, as well as methane, were selected for microbial intake and that the formation of unsaturated hydrocarbons is related to the consumption of C_{2+}.

4.3. Carbon isotopic composition of C_1–C_4 alkanes

Six cores from the WMF and DSPF were selected for a detailed study of the vertical distribution of the C_1–C_4 stable carbon isotopic composition ($\delta^{13}C$). The obtained data reveal significant variations in carbon isotopic composition within the ca. 50–100 cm sedimentary depth interval, consistent with the compositional changes of the gas as discussed in the previous sections. This leads to caution with regards to the stable carbon isotope data (Table 2).

Table 2
Stable carbon isotope compositions

Core No.	Interval (cm) bsf	Carbon isotopes				
		C_1	C_2	C_3	iC_4	nC_4
Western Moroccan field						
Jesus Bar-	10	−31	−27	−32	−25	−26
aza MV	30	−24	−31	−33	−27	−24
TTR10	50	−27	−30	−27	−29	−27
AT-231G	69	−30	−16	−31	−34	−26
	79	−32	−25	−27	−27	−22
	89	−28	−19	n/d	n/d	n/d
	Average	−29	−25	−30	−28	−25
Ginsburg	10	−54	−16	n/d	n/d	n/d
MV	30	−36	−12	n/d	n/d	n/d
TTR10	88	−42	−23	−22	−25	−24
AT-236G	135	−41	−24	−23	−26	−24
	Average	−43	−19	−23	−25	−24
Ginsburg	0	−35	−23	−22	n/d	n/d
MV	30	−44	−20	−22	−28	−30
TTR10	65	−41	−22	−22	−25	−24
AT-238G	85	−56	−30	−21	−27	−19
	105	−42	−23	−22	−25	−24
	142	−41	−24	−23	−26	−24
	162	−41	−24	−24	−26	−25
	182	−40	−24	−23	−26	−25
	Average	−43	−24	−22	−26	−24
Deep South Portuguese field						
Bonjar-	20	−51	−29	−23	n/d	n/d
dim MV	50	−64	−23	−13	n/d	n/d
TTR10	90	−62	−31	−18	−27	n/d
AT-226G	Average	−59	−28	−18		
Bonjar-	24	−51	−34	−25	−30	−27
dim MV	36	−63	−26	−27	−28	−22
TTR10	46	−57	−28	−26	−27	−25
AT-227G	75	−58	−24	−24	n/d	n/d
	141	−52	−28	−21	−28	−20
	161	−52	−29	−21	−28	−21
	195	−50	−28	−22	−28	−20
	Average	−55	−28	−24	−28	−22
Carlos	0	−23	n/d	n/d	n/d	n/d
Ribeiro	40	−50	−14	n/d	n/d	n/d
MV	60	−66	−20	−22	−26	−23
TTR10	136	−58	−25	−23	−27	−24
AT-243G	Average	−49	−20	−22	−26	−23

n/d, not determined.

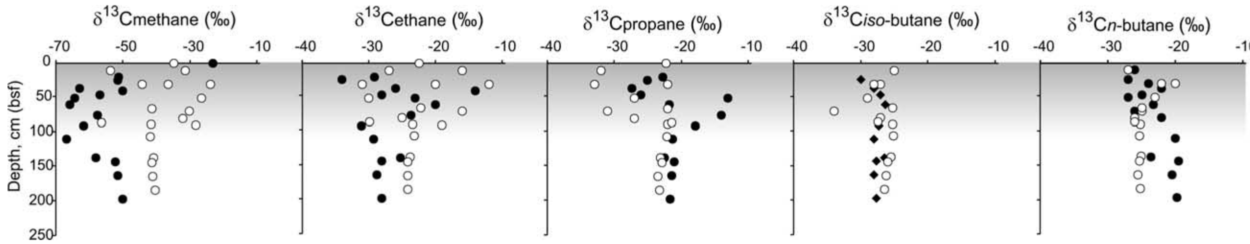

Fig. 7. Stable carbon isotope composition of C_1–C_4 alkanes as a function of depth. The gray area indicates interval with irregular $\delta^{13}C_{C2-C4}$ values which resulted from vital microbial actions. Black circles indicate samples from the DSPF, and white circles—from the WMF.

4.3.1. Methane

The methane carbon isotope composition ranges from −23 to −67‰ (Table 2). The heaviest $\delta^{13}C_{C1}$ values were obtained from the mud breccia of the Jesus Baraza MV (WMF) although the values are uneven along the core (see Table 2). The lightest values of $\delta^{13}C_{C1}$ were obtained from mud breccias of the Bonjardin MV (DSPF). Schoell (1983) proposed that the isotopic composition of methane is not significantly changed after its generation. The changes in isotope signature can be expected when the gas become mixed with another gas during migration (Schoell, 1983) or/and during microbial methane oxidation (Bernard, 1979), which is less likely to be significant at greater depth (James and Burns, 1984). Methane consumption, reflected in ^{13}C enrichment (Lebedew et al., 1969), is detected in the uppermost sediments from the Ginsburg, Jesus Baraza, Carlos Ribeiro, and the Bonjardim MVs. This correlates well with the methane concentration profiles (Fig. 4). In spite of the methane oxidation signature within the uppermost ~50–100 cm, Fig. 7 shows that the $\delta^{13}C_{C1}$ values differ between the WMF and the DSPF. This implies that the WMF and DSPF contain methane from two different sources.

4.3.2. Other light hydrocarbons (C_{2+})

The wet gas components also show a significant variability in $\delta^{13}C$ composition (Table 2). The $\delta^{13}C$ values of C_2 and C_3 have a range of −14 to −34‰ and of −13 to −31%, respectively. The highest scatter of the $\delta^{13}C_{C2-C3}$ values is observed within the uppermost ~50–100 cm (Fig. 7). Compared with C_2 and C_3 alkanes, the $\delta^{13}C$ values of iC_4 and nC_4 display less variability within this interval. Fig. 7 shows that the carbon isotope values of C_2–C_4 become more regular below ca. 100 cm bsf, which most likely indicates a reduction of microbial activity with depth.

5. Discussion

5.1. Compositional variations of C_{2+}

The relative proportions of C_1–C_4 *n*-alkanes in a gas sample provide an initial classification of the natural gas type and may identify the related microbial alteration of the gaseous components. Two molecular ratios, the gas wetness and the Bernard parameter, were applied for gas data to describe the compositional variations of the hydrocarbon gases from the two mud volcano provinces in the Gulf of Cadiz. Commonly, maximum gas wetness is associated with the peak of hydrocarbon generation (Stahl, 1977; Hunt, 1979), while microbial methane oxidation can result in similar (mature) gas wetness characteristics due to an increase of C_{2+} compounds (Coleman et al., 1981). Alternatively, microbial alteration of wet gas components can reduce gas wetness. Fig. 8 shows the compositional variations observed in hydrocarbon gases within the uppermost ca. 50–100 cm below sea floor (bsf). This interval is characterized by a great variability of the molecular gas composition due to diverse microbial actions. Within this interval, methane oxidation is reflected in a significant increase of the gas wetness and $C_1/(C_2+C_3)$ values, and vice versa, a decrease of the gas

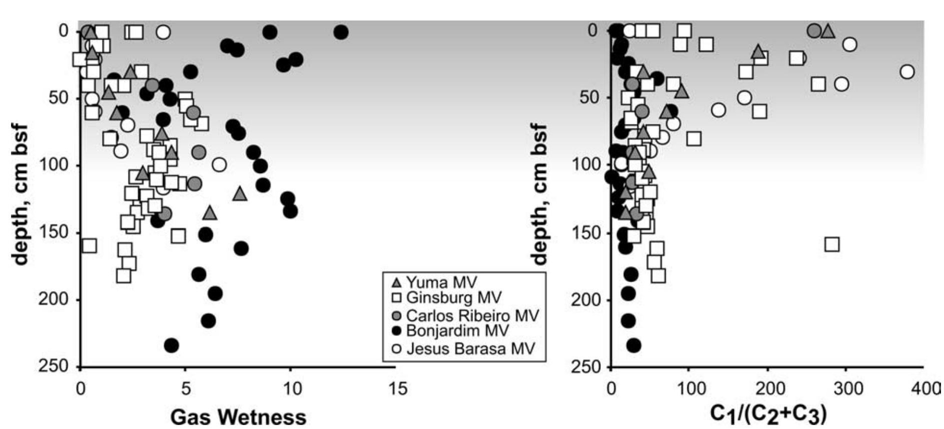

Fig. 8. Gas wetness and Bernard parameter as functions of depth. The gray area indicates interval where compositional variations in the hydrocarbon gases forced by microbial interactions are observed.

wetness and $C_1/(C_2+C_3)$ values most likely implies consumption/degradation of wet gas components (Fig. 8).

At the sediment surface the microbial activity, especially at seepage locations, is exceptionally high. Fluid fluxes frequently support highly diverse and productive ecosystems, thriving in response to different environments created by advection of migrated fluids. Microbially driven anaerobic/aerobic oxidation of methane and degradation of wet gas components can significantly modify the molecular and carbon isotope compositions of the initially migrated gas mixture. A prominent feature of most of the methane curves in the MVs of the Gulf of Cadis is a characteristic concave-up-shape (Fig. 4), considered to result from microbial methane consumption (Martens and Berner, 1974; Barnes and Goldberg, 1976; Reeburgh, 1976; Alperin and Reeburg, 1984). Remarkable, the wet gas components also show a decrease or even deficiency in the uppermost part of the sedimentary column (Fig. 5). Their distribution patterns are consistent with the C_1 'concave-up' curve geometry (Fig. 4). This implies that together with methane, C_{2+} gas components were also subjected to consumption.

Summarizing, the gas concentration data, their down-core distribution profiles, and their molecular ratios reveal that the studied mud volcano provinces in the Gulf of Cadiz are characterized by the presence of allochthonous gas with a high input of thermogenically formed hydrocarbons due to anomalous concentrations of C_{2+} gas constituents. The data also signify that the molecular composition and concentration of the gas are regulated by upward diffusion and biological oxidation within the subsurface at ca. 50–100 cm bsf. The latter indicates that in the studied locations migrated C_1 and C_{2+} components are consumed before they can escape into the overlying water column.

5.2. Genetic types of gases

To characterize the hydrocarbon gases from the two mud volcano provinces, we combined molecular concentrations, contents, and stable carbon isotope signatures of C_1–C_4 alkanes. As was shown in the previous sections, microbial activity in the uppermost 50–100 cm resulted in significant changes of concentrations, molecular and carbon isotope composition of the C_1–C_4 hydrocarbons in both the WMF and DSPF. The $\delta^{13}C$ values of C_1–C_4 alkanes below ca. 60 cm of the sediments do not seem to be significantly affected by in situ microbial actions. This suggests that hydrocarbon gas samples from the lower intervals could represent an 'original' gas mixture, thus containing information on the sources, maturity and microbial alterations in the deeper subsurface. Accordingly, for the characterization of genetic gas types gas data were used only from intervals below ca. 60 cm. The complete gas data though is also presented to the reader for the comparison.

Concentrations of methane and wet gas components in all studied locations of the Gulf of Cadiz are clearly anomalous (Figs. 4 and 5). Ethane and propane so far have never been generated in significant quantities by microbial processes (Oremland et al., 1988). Ethane, propane and butanes are formed primarily between 70 and 150 °C with peak generation around 120 °C (Hunt, 1995). High concentrations of C_{2+} especially C_4 and C_5 hydrocarbons are expected if thermogenic gases are present (Cline and Holmes, 1977; Sandstrom et al., 1983). This signifies that gases from both mud volcano provinces of the Gulf of Cadiz are characterized by input of thermogenic hydrocarbons from deeper sources. Besides, the down-core concentration profiles of C_1–C_4(C_5) hydrocarbons (despite their difference in concentration levels) show an absence of correlation with the TOC content, which also indicates an allochthonous nature of the gas to the hosting mud breccias.

Fig. 9 shows the Bernard diagram (Bernard et al., 1978; Faber and Stahl, 1984), modified by Whiticar (1994) to classify hydrocarbon gas. Two distinct genetic gas types can be recognized for the WMF and for the DSPF (Fig. 9a). Fig. 9b shows gas data from the lowermost parts of the sediments.

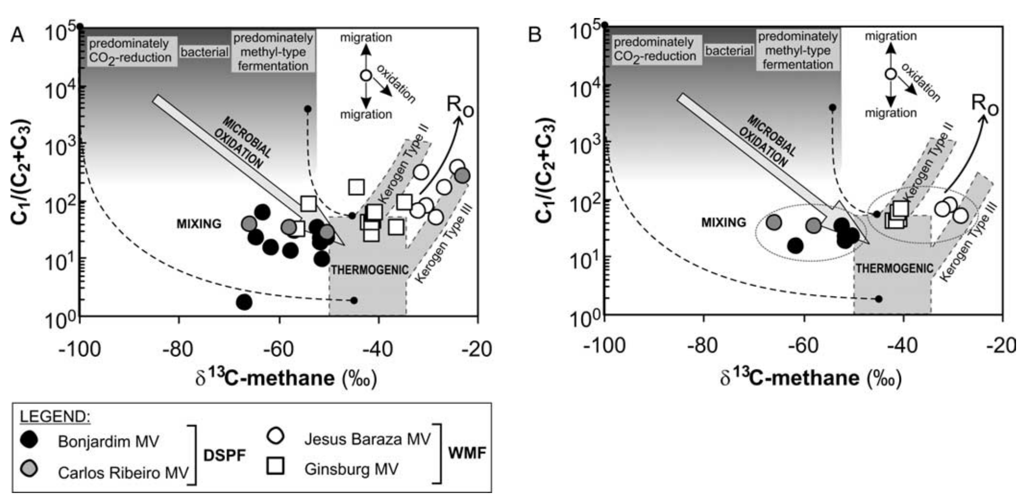

Fig. 9. Bernard diagram to delineate gas types (after Whiticar, 1994). Two different groups of gases in the WMF and DSPF are recognized. The WMF gas represents mature gases, (Ro < 1.2%), derived from kerogen type II and/or a mixture of kerogens of types II and III. The DSPF gas consists of a mixture of thermogenic and bacterial gases. (A) The complete suite of gas data; (B) the data from the intervals below 60 cm bsf.

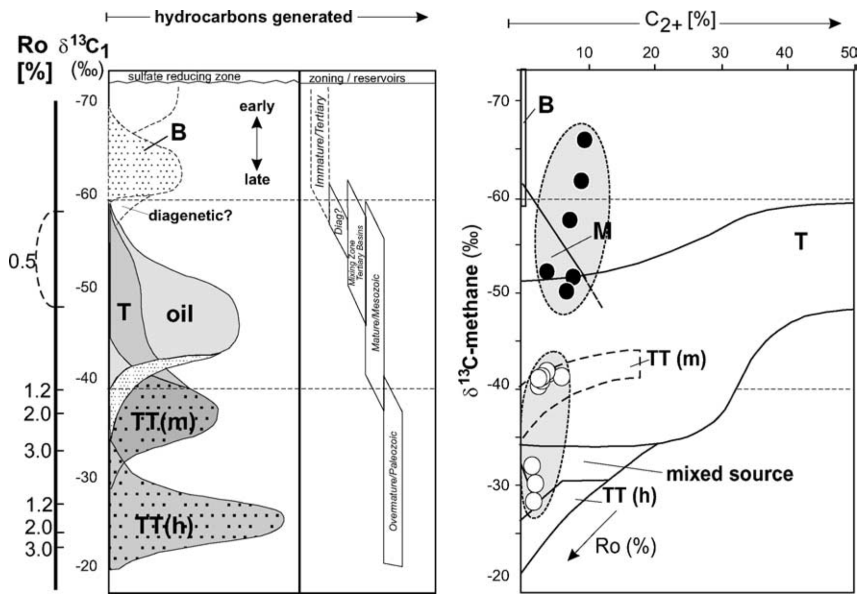

Fig. 10. Relative concentration of wet gas components in relation to stable carbon isotope composition of methane (after Schoell, 1983) showing two different gas groups in the WMF (white circles) and in the DSPF (black circles). Primary gases (B, bacterial; T, thermogenic associated; TT(m), non-associated dry gases from sapropelic liptinic organic matter; TT(h), non-associated gases from humic organic matter) are distinguished on the basis of fields determined by Schoell (1983). Mixing of primary gases (M, mixed gases) reflects in the different proportions of thermogenic and bacterial gases. The data set includes values from intervals below 60 cm.

The uppermost intervals, where microbial alteration of C_1–C_4 alkanes is taking place, have been excluded. As a result, two different gas groups are more clearly highlighted (Fig. 9b).

MVs from the WMF, the Ginsburg and the Jesus Barasa, depict mature gas characteristics with $\delta^{13}C_{C1}$ values ranging from −28 to −42‰ (Table 2). The C_{2+} content varies between 1 and 6% from the total hydrocarbon gases. Concurrently, MVs from the DSPF, the Bonjardim and the Carlos Ribeiro, are characterized by less mature gas signatures (Fig. 9). These gases have $\delta^{13}C$ values of methane between ca. −50 and −67‰ although the C_{2+} content ranges from 3 to almost 10%.

The stable carbon isotope composition of methane is dependent on type and maturity of the initial source (Galimov, 1968; Stahl, 1977, 1979). Migration and/or mixing may be a mechanism of carbon isotope fractionation, and is reflected in either enrichment or depletion with ^{12}C (Galimov, 1967; Lebedev and Syngayevski, 1971). Fig. 9 shows that the composition characteristic of gas from the MVs of the WMF falls in the 'thermogenic gas field'. Besides, the source, from which the gas was derived, is indicated on the diagram as kerogen of type II for the Ginsburg MV and as a mixture of kerogens II and III for the Jesus Baraza MV.

Hydrocarbon gas from the DSPF represents a mixture of gases of various origins. We consider that an admixture of bacterial gases is the reason for an immature characteristic of the methane, whereas, the relatively high content of wet gas components indicates the presence of thermogenic hydrocarbons (Fig. 9).

Using another principle for genetic characterization of gases outlined by Schoell (1983), two different gas groups can also be distinguished. Applying the same parameters (i.e. C_{2+} versus $\delta^{13}C_{C1}$), Schoell (1983) considered only three processes, maturation, mixing, and migration, which may influence the methane carbon isotope composition and C_{2+} concentration. In fact, the data (Fig. 10) confirm the interpretation of the Bernard diagram and also clearly indicate the presence of two different groups of gases in the WMF and DSPF. The WMF gas represents two mature gases, (Ro < 1.2%), derived from kerogen type II (the Ginsburg MV) and a mixture of kerogens of types II and III (Jesus Boraza MV). The DSPF gas is a mixture of thermogenic and bacterial gases with relatively immature characteristics (the beginning of the oil window; Ro ≤ 0.5%) (Fig. 10). In fact, the mature characteristics of the gas from the WMF coincide with geochemical data obtained from a gas reservoir in a faulted anticline in the Arkoma basin, Oklahoma (Stahl et al., 1981).

5.3. Secondary processes

5.3.1. Mixing

The evidence of gas mixing for both the WMF and DSPF is shown in Fig. 11, which reflects an almost linear relation between the C_{2+} contents and the $\delta^{13}C$ signatures of methane (Schoell, 1983). Mixing of gases of different origins is a common phenomenon (Whiticar, 1994), which indicates that gas components are not necessarily co-genetic. In a thermogenic co-genetic C_1–C_2 pair, methane is depleted in ^{13}C between 5 and 10‰ relatively to the ethane (Silverman, 1971; Deines, 1980). An admixture of a biogenic gas will be reflected in a significant carbon isotope difference between methane and the other wet gas components, i.e. methane will appear much lighter relative to C_2–C_4. The average value of $\delta^{13}C_{C1}$ in the DSPF is −57‰ while the average value of $\delta^{13}C_{C1}$ in the WMF

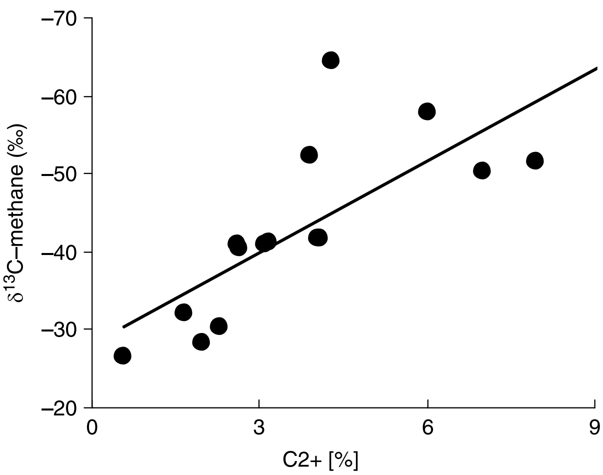

Fig. 11. Gases of mixed bacterial and thermogenic origin. Compositional variations are caused by various mixing proportions of the gases (after Schoell, 1983).

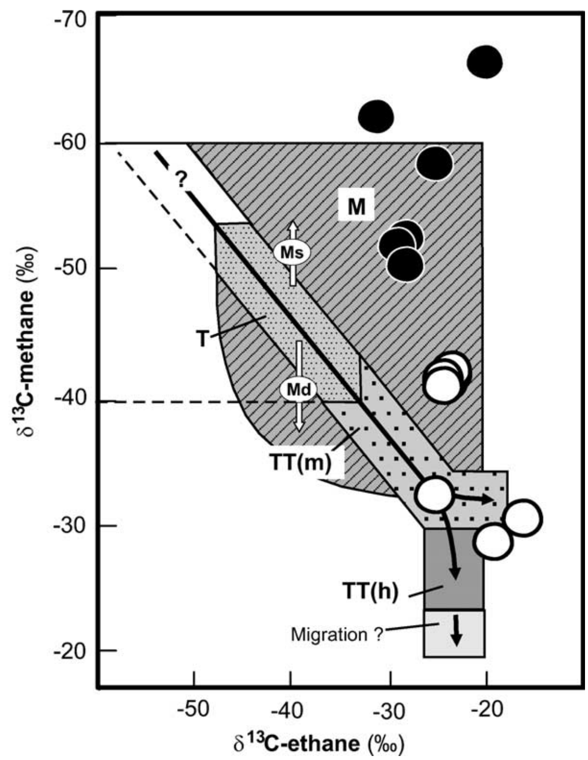

Fig. 12. Mixing/migration diagram. Genetical definition of hydrocarbon gas by relation of $\delta^{13}C$ changes in ethane and methane (after Schoell, 1983). Gas from the WMF (white circles) is characterized by mixture of two thermogenic gases. Gas from the DSFP represents a mixture of thermogenic and bacterial gases.

is −38‰ (Table 2). If a $\delta^{13}C$ of −70‰ is assumed for pure biogenic methane (Chung et al., 1988), a proportion of ca. 50% of biogenic gas in DSPF can be calculated as mixed with thermogenic gas of −30‰ (Schoell, 1983) from humic source materials. Nevertheless, it is difficult to recognize the source or sources for the methane from the DSPF. Mixing of early formed biogenic gas and later formed thermogenic gas results in a lack of abilities to differentiate the thermogenic gas due to compositional changes caused by mixing (Rice and Claypool, 1981). Besides, the earliest formed thermogenic methane is isotopically light, $\delta^{13}C$ values are −55‰ (Sackett, 1978; Stahl et al., 1979).

Fig. 12 shows that in general methane is not co-genetic with ethane. Besides, the $\delta^{13}C$ values of ethane from the DSPF are on average −27‰, which is the signature of ethane in mixed gases (Mattavelli et al., 1983). In contrast, the ethane from the WMF has a more positive carbon isotopic composition, on average −23‰. Furthermore, the C_1–C_2 pair from the Ginsburg MV demonstrates a close relation between methane and ethane on the basis of the small differences in their carbon isotopic compositions (Table 2). The decrease in $\delta^{13}C$ difference between C_1 and C_2 is a result of an increase of the thermal maturity (James, 1983). This is consistent with Fig. 10, showing mature characteristics of the gas from the Ginsburg MV.

5.3.2. Microbial alteration

The level of maturity and the original gas source is reflected in the carbon isotopic composition of C_2–C_4 gas components (James, 1990). Microbial alteration extensively affects the maturity relationship as shown in the $\delta^{13}C$ signal of gaseous alkanes, especially in the topmost decimeters of marine sediments. In unaltered gases, the carbon isotopic compositions of C_1–nC_4 (excluding iC_4) follow a smooth progression from C_1 to nC_4 (James, 1983), which is not the case for our gas data set (Table 2). Mud volcanoes form both provinces show reduction of ethane, which is reflected in its ^{13}C enrichment (Table 2). Anomalously, enriched ethane was detected in the topmost parts of the Ginsburg MV (WMF) and Carlos Ribeiro MV (DSPF), which is in conjunction with ethane concentration profile indicating its consumption in the uppermost decimeters of sediments (Table 2, Fig. 5). In this aspect, obtained ethane data partly supports the findings of Clayton et al. (1997); Pallasser (2000), where authors showed most positive $\delta^{13}C$ values of ethane as a consequence of its microbial alteration together with relatively unaltered $\delta^{13}C$ signatures of propane (Clayton et al., 1997; Pallasser, 2000). Enriched in ^{13}C ethane was detected in the deeper intervals from the Jesus Baraza MV (WMF), which is probably also result from selective uptake of this alkane by unknown type of ethane-degrading microorganisms.

In contrast, James and Burns (1984) reported microbial alteration of subsurface reservoired gas by the selective removal of propane. This resulted in an anomalous heavy propane carbon isotopic composition and ethane was relatively unaffected (James and Burns, 1984). In the unaltered gases, the $\delta^{13}C$ values of propane constitute ca. −27 to −28‰ (James, 1983). Hence, both the WMF and the DSPF, also show propane alteration, $\delta^{13}C_{C3}$ comprises by a mean −23 and −21‰, respectively (Table 2). Except sediments from the Bonjardim MV, $\delta^{13}C$ values of propane remain similar along the sediments. This can imply that measured propane was microbially changed in the subsurface before it was transported by fluid upward.

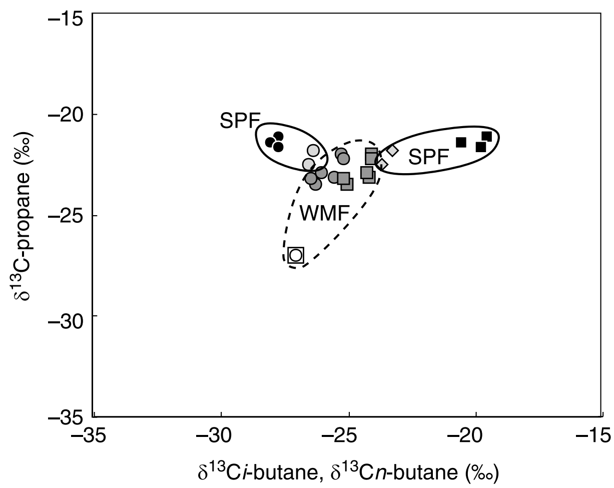

Fig. 13. Relationship of carbon isotope ratios for propane versus *i*-butane and *n*-butane. *iso*-Butane/propane—DSPF: Bonjardim MV (●); Carlos Ribeiro MV ( ); WMF: Ginsburg MV (◎); Jesus Baraza MV (○). *n*-Butane/propane—DSPF: Bonjardim MV (■); Carlos Ribeiro MV (▣); WMF: Ginsburg MV (□); Jesus Baraza MV (◎). The data set includes selection of values below ca. 60 cm.

Microbial alteration is also clearly illustrated in the butane dataset (Fig. 13). Although the $\delta^{13}C$ values of *iso*- and *n*-butanes are generally in the same range in the gases from both mud volcano provinces, the butanes from the DSPF display a greater variability in their $\delta^{13}C$ values (Fig. 13; Table 2). Hence, the isotopically heavy values of *n*-butane from the DSPF suggest that there has been a reduction of nC_4 likely as a result of its microbial consumption. In contrast, butanes from the WMF have relatively steady stable carbon isotope characteristics, indicating their possible co-genetic nature and absence of a microbial alteration signal.

Thus, propanes from both locations and *n*-butane from DSPF have been microbially altered in the deeper subsurface, which makes the interpretation of their maturity/sources difficult.

5.4. Geological and tectonic controls

Both the WMF and the DSPF are located within the olistostrome unit representing huge allochthonous deposits emplaced in the Gulf of Cadiz in the late Tortonian (Maldonado et al., 1999; Somoza et al., 1999). Taking into consideration the sedimentary cover and the present structure of the Gulf (Medialdea et al., 2004), it is quite possible that olistostrome deposits could possess subsurface gas accumulations, representing a re-deposited mixture of hydrocarbons migrated from below. The sediments of the olistostrome masses include Miocene units from Langhian to Messinian and are composed of various clays with some intervals of limestone and sand lenses (Maldonado et al., 1999). MVs from the DSPF appear within the central domain of the olistostrome (Fig. 1), which includes the complete Miocene depositional sequences and constitutes the bulk of the sedimentary infill of the slope basis including fragments of Mesozoic and plastic Triassic materials (Medialdea et al., 2004). The area is characterized by compressive deformation, thrusting and the presence of deep faults which could act either as pathways for fluid migration or as a structural trap for hydrocarbons, or may provide a link between sedimentary units from different stratigraphic horizons with different physical properties.

The tectonic regime in the Eastern domain of the olistostrome, where the WMF is located, is different. Here, extensive mud diapirism and mud volcanism is a characteristic feature. The Yuma, Ginsburg, Jesus Baraza, and the Rabat MVs have a linear orientation, reflecting their relation with a NW–SE orientated strike-slip fault system observed on the seafloor (Gardner, 2001). The trend of this fault system is coherent with the direction of convergence between the African and the Eurasian plates (Diaz-del-Rio et al., 2003), suggesting that mud volcanism and mud diapirism is triggered by the tectonic forces related to plate movements (Gardner, 2001).

5.5. Migration

The presence of particular tectonic regimes in the Gulf of Cadiz may be additional evidence for the presence of mixed hydrocarbon gases. Mattavelli et al. (1983) stated that formation of mixed gases appears generally bound to areas of faulting. The hydrocarbon gas from both mud volcano provinces is relatively dry, with C_{2+} contents in the WMF and in the DSPF of on average 3 and 8%, respectively. Predominance of woody-coaly organic matter (i.e. kerogen type III) over the more lipid-rich oil-prone sources (i.e. kerogen type II) can be a reason for high production of dry gas. In contrast, migration can be important for redistribution of hydrocarbons due to their apparent diffusion coefficients (Leythaeuser et al., 1980, 1984). This leads to the C_{2+} depletion, and therefore, dry gas characteristics (Silverman, 1971). Migration processes, without any doubts, were active in the past and are still active at present in the Gulf of Cadiz. The occurrence of MVs is already ample corroboration of vertically focused fluid transport. Vertical-migration distances in the Gulf of Cadiz can be considerable, depending on vertical faulting, changes in permeability as a result of facies variation, possibilities of combined vertical and lateral migrations, active tectonics, etc. However, as a consequence of both tectonic disruption and facies changes, related to the past and present tectonic events in the Gulf, the lateral continuity of migration-carrier beds should be relatively poor. This indicates a lack of long-distance lateral migration of deep generated hydrocarbons from the DSPF to the WMF. Different tectonic regimes and thicknesses of the sedimentary cover in the central and the Eastern domains of the olistostrome (Medialdea et al., 2004) also suggest a distinctive level and distribution of heat flow, which is one of the main factors causing hydrocarbon generation. For that reason, the same sedimentary unit may show different maturity characteristics in the DSPF and in the WMF. In this context, the identified gas types may belong to the same source beds, being under a different heat stress within these two MV provinces. As shown above, both gas types are dry gases with generally similar C_{2+} compositions.

5.6. A possible locality of hydrocarbon gas accumulations

An independent geochemical study of rock clasts from the Yuma MV (WMF) shows generally immature characteristics of kerogen belonging to the types II and III (Kozlova et al., 2004) which is consistent with the kerogen types established for the hydrocarbon gas in the area. The age of these rock clasts varies from the middle Eocene to the late Miocene (Ovsyannikov et al., 2003), which is consistent with the age of the olistostrome deposits (Maldonado et al., 1999). The contrast between maturities of the clasts and the gas, however, may indicate that the source rocks with similar kerogen types belong to deeper horizons, since the gas generation window locates from ca. 105–155 to 175–220 °C (Pepper and Corvi, 1995). It implies possible redeposition of migrated thermogenic gas within the olistostrome or/and even within the Pliocene-quaternary sediments in the WMF.

Gas from the DSPF represents a mixture of thermogenic and biogenic gases as reflected by its immature signal. This also may indicate redeposition of the migrated/mixed gas at shallow depths, possibly within the olistostrome or/and Pliocene-quaternary units.

In addition, the recognized microbial consumption of propanes in both areas and *n*-butane in the Bonjardim MV (DSPF) is an additional confirmation of secondary processes, which may occur in the deep subsurface. Similar gas alterations were reported in the reservoired hydrocarbon gas and also in a variety of geological settings, both onshore and offshore (James and Burns, 1984).

6. Conclusions

The Gulf of Cadiz is an area of active mud volcanism and fluid venting. This implies active processes of fluid migration from the deep-sited horizons. MVs from two provinces, WMF and DSPF, have been studied to identify peculiarities of hydrocarbon gas composition, to classify hydrocarbon gases to their types/maturity, possible sources, and to trace their alteration due to secondary effects, such as migration, mixing, diverse microbial actions or combination of them. Obtained results revealed that among studied MVs, the Ginsburg and the Yuma are the most active structures currently known in the Gulf of Cadiz.

The molecular gas composition shows relatively dry gas characteristics; the C_{2+} content is 3 and 8% in the WMF and the DSPF, respectively. Changes in gas composition and curves of concentration profiles from both MV areas show (i) absence of strong upward gas transport and (ii) active biological processes within ca. 50–100 cm bsf. This means that in the studied locations C_1 and C_{2+} are consumed before they can escape into the overlying water column.

The combination of gas concentration data, stable carbon isotope composition of C_1–C_4 alkanes, and molecular ratios revealed the presence of two different groups of gases in the WMF and DSPF. Both gas groups represent allochthonous to the erupted mud breccia gas with high input of thermogenically formed hydrocarbons as shown by anomalous concentrations of C_{2+} gas components. The WMF gas represents mature gases ($Ro < 1.2\%$) derived from kerogen type II (the Ginsburg MV) and a mixture of kerogens of types II and III (Jesus Boraza MV). The DSPF gas is a mixture of thermogenic and bacterial gases which cause of its relatively immature characteristics (the beginning of the oil window; $Ro \leq 0.5\%$). A source and maturation characteristic of gas from the DSPF is difficult to determine due to migration, biodegradation, and mixing processes.

The combination of molecular and stable carbon isotopic signatures of the C_1–C_4 alkanes provides geochemical evidence that besides methane, C_2–C_4 hydrocarbons can be also microbially consumed within first decimeters below the seafloor. Further, microbial activity in the first top ca. 60 cm reflects in the formation of unsaturated ethene and propene which appearance coincided with the vanishing of saturated hydrocarbon gases.

Microbial consumption of ethanes and propanes in both areas and of *n*-butane in the Bonjardim MV (DSPF) makes identification of source and maturity for these alkanes difficult. Simultaneously, it can be an indicator of secondary microbial processes previously observed in suite of natural gases (James and Burns, 1984; Clayton et al., 1997; Pallasser, 2000) and seepages (Sassen et al., 2004).

The studied MVs appear within the olistostrome body, the WMF is located in the Eastern domain and the DSPF—in the central part. Different tectonic regimes and thicknesses of the sedimentary cover within the olistostrome domains (Medialdea et al., 2004) suggest distinctive fluid venting environments as well as distinctive distribution patterns of heat flows. This should be reflected in the geochemical behavior/properties of migrating fluids, which is consistent with the different peculiarities of the erupted mud breccias and the recognition of two gas groups in the WMF and DSPF. This study reveals that despite the discrete maturation characteristics, both gas types are a complex of secondary migrated, microbially altered and mixed hydrocarbons, most likely redeposited within the olistostrome/Pliocene-quaternary sedimentary units. It may possibly imply the existence of hydrocarbon accumulations in the subsurface and probable association of mud volcanoes with the olistostrome body.

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