

Sea-floor features related to hydrocarbon seeps in deepwater carbonate-mud mounds of the Gulf of Cádiz: from mud flows to carbonate precipitates

R. León · L. Somoza · T. Medialdea · F. J. González ·
V. Díaz-del-Río · M. C. Fernández-Puga · A. Maestro ·
M. P. Mata

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Abstract Underwater images taken from deepwater carbonate-mud mounds located along the continental margin of the Gulf of Cádiz (eastern Central Atlantic) have identified a great variety of hydrocarbon seep-related geomorphic features that exist on the sea floor. An extensive photographic survey was made along the Guadalquivir Diapiric Ridge, after detailed examination of the

main mounds identified on previous swath bathymetry coverage, high-resolution seismic imagery, dredge and gravity core data. Recognised fluid-induced geomorphic features include seep precipitates, named here generically as hydrocarbon-derived authigenic carbonates (HDACs), mud-breccia flows and piping/rills, at scales ranging from metres to centimetres. Based on the viscosity, texture, morphology, and the nature of observed features, we have categorized the geomorphic seeps into the following types: mud-breccia flows and liquid seepages, which can be grouped as highly viscous and viscous mud-breccia flows, gassy mud-breccia flows, and small-scale piping/rills; HDACs types, including massive crusts, “honeycombed” carbonate crusts, nodular aggregated crusts, steeply dipping to vertical slabs, and pipe-like formations (chimneys). These widespread geomorphic features observed along the carbonate-mud mounds reveal alternate periods of (1) active mud-flow extrusion (mud-volcano formation), (2) reduced seepage activity, with the formation of extensive carbonate features by chemosynthetic organisms, and (3) formation of hardgrounds and colonisation by non-chemosynthetic organisms such as deepwater corals (e.g. *Lophelia pertusa*, *Madrepora oculata*). The formation of large amounts of HDACs is related to the microbially mediated oxidation of hydrocarbon fluids (biogenic and thermogenic) during periods of slower fluid venting. This has led to the hypothesis that these carbonate-mud mounds could be built up by alternating episodes of varying fluid-venting rates, with peaks that may have been triggered by tectonic events (e.g. high-seismicity periods) and slower rates controlled by climate/oceanographic factors (e.g. glacial to interglacial climatic transitions, increasing shallow subsurface hydrate formation, and sealing of sea-floor fluid venting).

R. León (✉) · L. Somoza · T. Medialdea · F. J. González ·
M. C. Fernández-Puga · A. Maestro
Marine Geology Division, Geological Survey of Spain (IGME),
Rios Rosas 23, 28003 Madrid, Spain
e-mail: r.leon@igme.es

L. Somoza
e-mail: l.somoza@igme.es

T. Medialdea
e-mail: t.medialdea@igme.es

F. J. González
e-mail: fj.gonzalez@igme.es

M. C. Fernández-Puga
e-mail: mc.fernandez@igme.es

A. Maestro
e-mail: a.maestro@igme.es

V. Díaz-del-Río
Centro Oceanográfico de Málaga,
Instituto Español de Oceanografía,
29640 Málaga, Spain
e-mail: diazdelrio@ma.ieo.es

M. P. Mata
Facultad de Ciencias del Mar, Universidad de Cádiz,
Puerto Real, 1510 Cádiz, Spain
e-mail: pilar.mata@uca.es

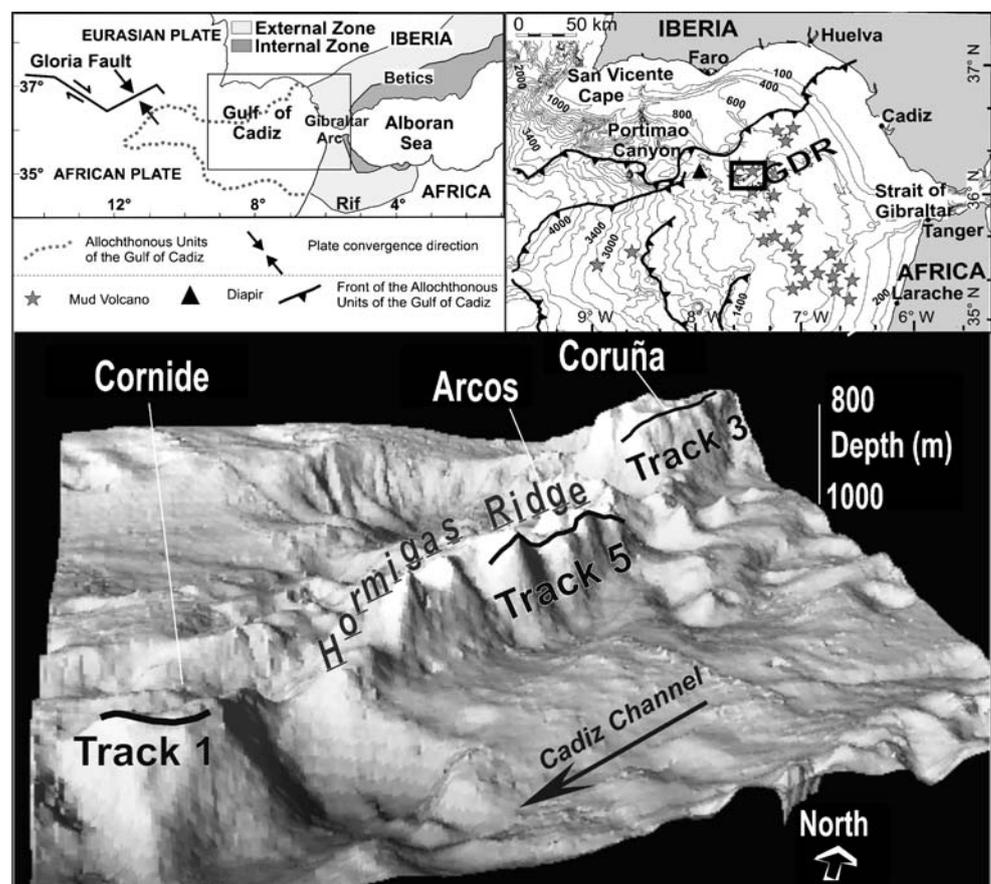
Introduction

A variety of seep-related geomorphic features has been described on the sea floor, including precipitates (carbonates and hydrates), pockmarks, piping/rills, brine pools, and mud volcanoes (e.g. Milkov 2000; Dimitrov 2002). Although numerous fluid expulsion features have been identified in diverse tectonic settings, there is still little information on the distinct processes and factors that form and control them. Some factors are evident, such as the chemistry of expelled fluids, and the rates and duration of the fluid flow. As a first approach, the accumulation of sediment in the form of cones, such as mud volcanoes, has been related to the rapid expulsion of fluids, whereas slow seepage promotes lithification of the sea floor through precipitation of a variety of mineral species (e.g. Roberts 2001). Another factor to consider is the tectonic setting. For instance, along convergent margins, variations in the regional compressional stress field strongly influence the source, pressure and temperature of the underlying fluids, causing fluid flows of varying viscosity and, therefore, different sediment degassing morphologies on the sea floor (e.g. Mediterranean Ridge: Ivanov et al. 1996; Costa Rica: Bohrmann et

al. 2002; Nankai wedge: Henry et al. 2002). Otherwise, the most important process in “transforming” hydrocarbon fluid seeps is the microbially mediated anaerobic oxidation of hydrocarbons (Boetius et al. 2000) and precipitation of ^{13}C -depleted carbonates as by-products (e.g. Hovland 1990; Stakes et al. 1999; Peckmann et al. 2001; Aloisi et al. 2002; Stadnitskaia et al. 2006).

The importance of hydrocarbon-related seeps in the Gulf of Cádiz (Fig. 1) was obscure until the recent advent of new technologies such as multi-beam echosounders and long-range side-scan sonars for deep marine exploration. Cooperation between the IOC-UNESCO “Training Through Research” (TTR) cruises and the Spanish “TASYO” project led to the discovery of what probably are the largest fields of hydrocarbon-derived authigenic carbonates (HDACs) in the form of chimneys, crusts and slabs (Díaz-del-Río et al. 2003). Several cruises were carried out aboard the research vessels *Prof. Logachev*, *Hespérides* and *Cornide de Saavedra* from 1999 to 2005 in the Gulf of Cádiz (Somoza et al. 2002). Data collected during these cruises revealed a large number of new sea-floor structures related to hydrocarbon fluid venting in this active tectonic region (Ivanov et al. 2000; Somoza et al.

Fig. 1 Geological setting of the Gulf of Cádiz, showing the location of sea-floor structures related to hydrocarbon seepages studied in this paper. Three-dimensional bathymetric image showing photo-tracks of the Anastasya-01 cruise over the main carbonate-mud mounds of the Guadalquivir Diapiric Ridge (GDR): Cornide (track 1), Coruña (track 3) and Arcos (Hormigas Ridge, track 5)



2000; Gardner 2001). Scientists aboard the Belgian research vessel *Belgica* identified, in May 2002, a cluster of giant shallow-water mud volcanoes on the Atlantic margin of Morocco (Van Rensbergen et al. 2005). In December 2003, Kopf et al. (2004), aboard the German research vessel *Sonne*, surveyed and filmed most of the seeps identified in previous cruises.

The origin of hydrocarbon-related fluid-venting structures in the Gulf of Cádiz is associated with compressional and salt tectonics that affect the so-called Olistostrome Mass in response to the Africa-Eurasia plate convergence (Maldonado et al. 1999; Medialdea et al. 2004). The close relationship observed between the tectonic structures and hydrocarbon-derived features suggests that fluid venting is triggered by the formation of pressurized compartments developed beneath thrust structures, which provide conduits for hydrocarbon-enriched fluids (Lowrie et al. 1999; Maestro et al. 2003). Three main types of fluid-venting geomorphic features, at different scales ranging from kilometres to hundreds of metres, have been reported in the Gulf of Cádiz: (1) pockmarks (Baraza and Ercilla 1996; León et al. 2005), (2) mud-volcano fields, some bearing gas hydrates on both the Iberian (Somoza et al. 2002; Pinheiro et al. 2003) and the Moroccan margins (Ivanov et al. 2000; Gardner 2001; Kopf et al. 2004; Van Rensbergen et al. 2005), and (3) carbonate-mud mounds, bearing huge amounts of carbonate chimneys, crusts and slabs related to diapiric ridges (Díaz-del-Río et al. 2003; Magalhães et al. 2004; Fernández-Puga et al. 2007), and characterised by high backscatter in side-scan sonar imagery. Sampling has shown that high backscatter values are related to high abundances of carbonate chimneys and crusts on top of these ridges (Díaz-del-Río et al. 2001; Somoza et al. 2003). Recently, diapiric ridges and related carbonate-mud mounds have also been described along the Moroccan margin (Van Rensbergen et al. 2005).

This paper describes the wide variety of hydrocarbon seep-related geomorphic features observed on deepwater carbonate-mud mounds in the northern sector of the Gulf of Cádiz, such as mud flows, seepages and biomineralization products. Although we focus on the analysis of underwater images of the carbonate-mud mounds in this sector of the Gulf of Cádiz, we also present a review of geophysical, geochemical and mineralogical data to develop an evolutionary model of the growth of these hydrocarbon-derived carbonate mounds.

Materials and methods

During the TASYO/2000 and the Anastasya-99, Anastasya-00 and Anastasya-01 cruises aboard B/O *Hesperides* and V/R *Cornide de Saavedra*, an extensive new dataset was acquired along more than 2,000 km. The study area

(8,500 km²; see Fig. 1) was extensively surveyed with multi-beam echosounders, multi-channel and very high-resolution reflection seismics, underwater cameras, and sampled by dredging and gravity coring.

Nearly 1,500 (1,452) underwater photographs were taken during the Anastasya-01 cruise over the main carbonate-mud mounds of the Guadalquivir Diapiric Ridge (GDR): 518 on track 1, 712 on track 3 and 222 on track 5 (Fig. 1). A towed Benthos-372 camera with a flash of 100-W power (Benthos-382) was used. The camera was fixed perpendicular to the sea floor; the flash, tilted with respect to the camera, was prepared for 6 m convergence with the sea floor. Interval shot was 10 s, the shutter open at 6/7 of the diaphragm, and the depth of field from 3.3 to infinity. Two types of films were used: Kodak-Tri-X-Pan for black and white photographs (tracks 1, 2 and 3), and Kodak-Ektachrome for colour photographs (tracks 4 and 5). A scale and compass were fixed to the underwater camera.

Photographic tracks were made following a detailed Simrad EM12S-120 swath bathymetry survey (Fig. 1). This system operates at a main frequency of 13 kHz, with 81 beams that allow a maximum coverage angle of 120° (about three times water depth). This system, triggered with a range of pulse lengths from 2–10 ms, has a vertical resolution of 0.6 m. CTD and SIPPICAN depth-temperature measurements of the water column were made with a precision of ±0.15°C.

Results

Three main mounds were surveyed with the underwater camera along the Guadalquivir Diapiric Ridge (GDR in Fig. 1): two main mounds, named Cornide (track 1) and Coruña (track 3), and an alignment of minor mounds named as the Hormigas Ridge (Fig. 1), the Arcos mound being the most prominent (track 5). Cornide and Coruña are flat-topped structures, whereas the Hormigas Ridge is made up of small conical edifices. The Guadalquivir Diapiric Ridge ranges from 800 to 1,100 m depth with a vertical relief of 250 m above the sea floor, and an asymmetric profile marked by steep slopes of 22–25° on the southern side and 12–15° on the northern side (Fernández-Puga et al. 2007). This ridge acts as a barrier that channels the Mediterranean Outflow Water (Hernández-Molina et al. 2003). Dredges from the Cornide and Coruña mounds collected large quantities of different types of carbonate chimneys (Díaz-del-Río et al. 2003). At the same time, gravity cores from these mounds yielded highly sulphidic sediments, with scattered crystals of pyrite, chemosynthetic fauna such as *Pogonophora* sp., and evidence of degassing structures forming typical “mousse-like” muds (Somoza et al. 2003). In contrast, dredges from the Hormigas Ridge

showed large clasts of carbonate crusts with scattered chimneys and dead coral rubble, mainly *L. pertusa*. Detailed analyses of the photographic tracks, and their correlation with the different types and characteristics of sediments and carbonates recovered through coring and dredging, allows us to categorize the seeps into the following geomorphic types:

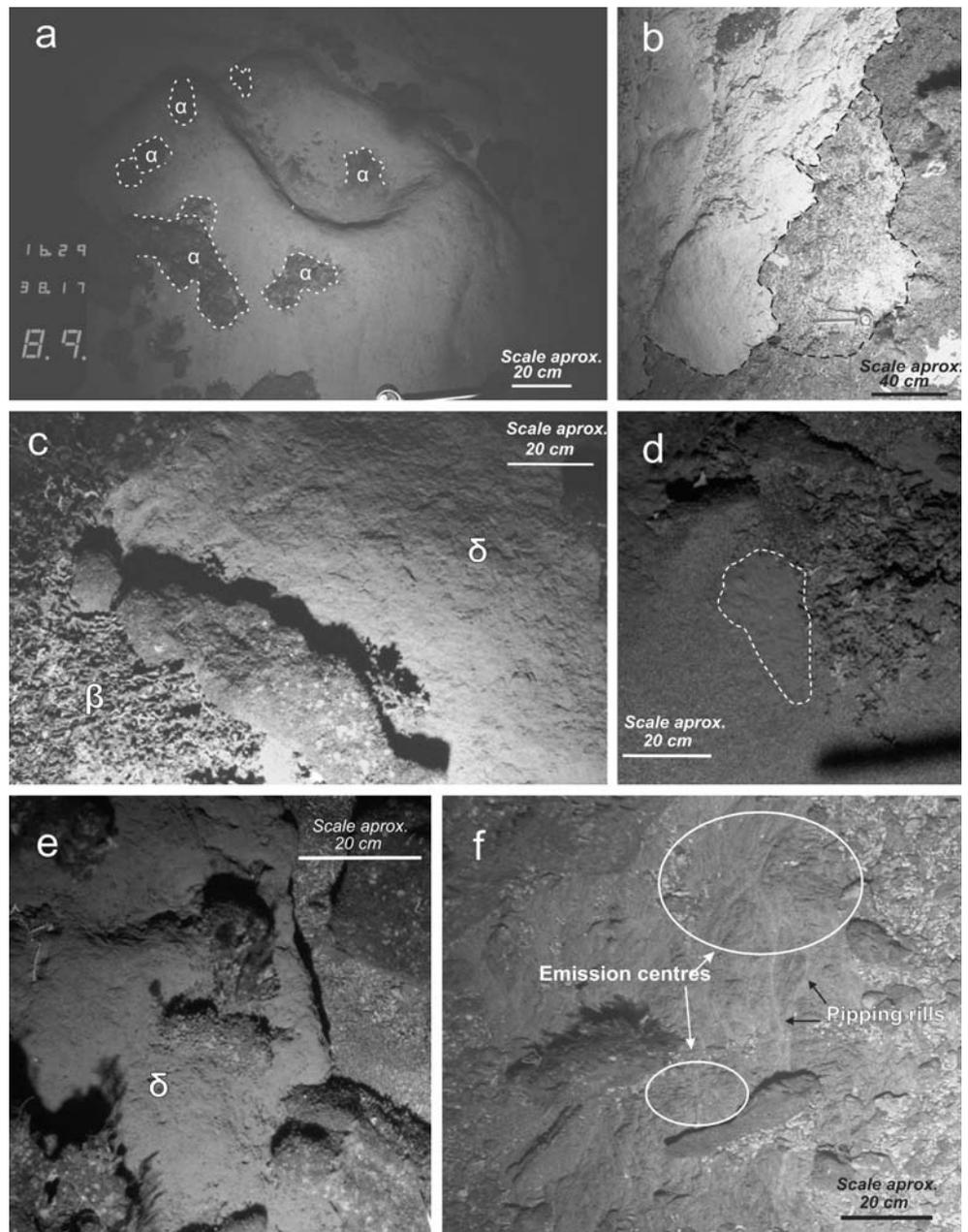
- Mud-breccia flows and liquid seepages that can be grouped as (1) highly viscous and viscous mud-breccia flows, (2) gassy mud-breccia flows, and (3) small-scale piping/rills; and

- A variety of HDAC types including (1) massive crusts, (2) “honeycombed” carbonate crusts, (3) nodular aggregated crusts, (4) slabs, and (5) pipe-like formations (chimneys).

Mud-breccia flows and liquid seeps: types and morphologies

Mud-breccia flows have been observed mainly on the Hormigas Ridge and on minor cones that surround the base of the main mounds, such as the Coruña mound (Figs. 1

Fig. 2 **a** Highly viscous mud-breccia flow and embedded fragments of carbonate crust (α), track 5. **b** Different episodes of viscous mud-breccia flows, Coruña mound, track 3. **c** Fragments of HDACs and gassy mud-breccia flows (δ) surrounded by dead coral rubble of *L. pertusa* (β), track 5. **d** Sea-floor textural aspect due to liquid seepages, track 5. **e** Surficial aspect of gassy mud-breccia flows (δ), track 5. **f** Piping/rills radial pattern of liquid seepages, track 5 (see Fig. 1 for track locations)



and 2). Dredges yielded large clasts (30–50 cm) of Lower-Middle Miocene blue marls (Maldonado et al. 1999), embedded in hydrogen sulphide muds. This mud breccia may be associated with the highest cone-shaped edifices observed along the Hormigas Ridge, and also to those found at the foot of the Coruña mound (Fig. 1). These circular structures also show high backscatter values and are surrounded by crater-like depressions. They resemble other mud volcanoes reported from nearby areas, such as the Anastasya mud volcano (Somoza et al. 2003), even though its size is much smaller. These structures are topographically expressed as sea-floor cone-shaped edifices built up by several episodes of mud-breccia flows generated by mud and fluid eruptions (water, brine, gas, oil) as a result of degassing processes in deeper reservoirs (Fernández-Puga et al. 2000). The slopes of the cones observed on the Hormigas Ridge show a wide range of values, 1–20°. Although these edifices are not as large as in other areas, the cones observed along the Hormigas Ridge seem to be associated with the most recent periods of mud-flow ejections.

Three main types of geomorphic expression of outflows have been observed in the underwater camera images: (1) highly viscous and viscous mud-breccia flows, (2) gassy mud-breccia flows, and (3) small-scale piping/rills from liquid seepages. We propose that the variability observed in the slope angle in the mud-flow features could result from the following factors:

- Variations in shear strength of the mud flows, and
- Rate of mud-flow cementation caused by methane-derived authigenic carbonates.

Highly viscous and viscous mud-breccia flows

Highly viscous and viscous mud-breccia flows comprise a group of very dense and viscous mud flows, containing numerous clasts embedded in stiff mud that form dome-like edifices with steep slopes. These outflows constitute an auto-breccia of extrusive muddy materials in which there are frequent carbonate crust fragments; these are probably related to ejection by cataclastic flow (Fig. 2a,b).

Highly viscous flows are massive extrusions where it is not possible to distinguish any structure and therefore, to delineate distinct outflow episodes. The high viscosity of such flows generates a dome-like cone with very steep slopes ranging from 15 to 20° (Fig. 2a). Besides, we have observed, in several mud volcanoes, the occurrence of domes with very steep slopes (10–13°) that taper the top of the volcanic edifice, interpreted as produced by highly viscous flows (e.g. Anastasya mud volcano in Somoza et al. 2003).

On the other hand, in the viscous flows it is possible to distinguish, by their colour contrast, different outflow

episodes that moved downslope (Fig. 2b). In this sense, whitish flows do not show the presence of sessile organisms on their surfaces, and they are presumed to be the most recent flows, whereas the greyish ones are associated with major colonisation by benthic organisms. The plastic behaviour of the viscous mud breccia is reflected by deformation on the surface (Fig. 2b).

Gassy mud-breccia flows

This type of flow is represented on the sea floor by smooth muddy patches with a “mousse-like” texture that are not colonised by sessile organisms (Fig. 2c,e). This texture has been also observed in cores taken from the Cornide mound (Somoza et al. 2003). It reflects a very porous composition related to degassing processes, e.g. the presence of hydrogen sulphide (H₂S) and chemosynthetic fauna (*Pogonophora* sp. tubeworms). This characteristic texture has also been related to hydrate dissociation in other sectors of the Gulf of Cádiz (Pinheiro et al. 2003). Even though this type of texture might be related to degassing after hydrate destabilisation, we do not have direct evidence of hydrates on or beneath sea-floor sediments in photographs of this area. In contrast, evidence of methane micro-seep activity related to this type of outflow has been inferred by the presence of scattered colonies of *Pogonophora* sp. and *Calyptogena* sp. (Kopf et al. 2004).

Gassy mud-flow features are observed both ejecting through lineated fissures (Fig. 2e) and as “sedimentary lobes” overlying the surrounding sediments (Fig. 2c). They are composed mainly of dead coral rubble (“β” in Fig. 2c) and fragments of carbonate crusts. Dead coral rubble consists of many small, broken coral pieces and coral branches up to 30 cm high, belonging to species such as *L. pertusa*, *M. oculata* and *Desmophyllum* sp. (Kopf et al. 2004). Several gastropods, brachiopods and small hydrozoans are attached to the dead coral pieces. Isolated living corals growing on the scattered blocks of the carbonate crust are also observed surrounding the muddy patches (Fig. 2e).

Small-scale piping/rills (liquid seepages)

This type is characterised by small-scale (30–50 cm) radial flow patterns with a channelled rill-type texture that is clearly distinguished over the surrounding sea-bottom sediments (Fig. 2d,f). The most recent radial flows show no colonisation of sessile organisms, in contrast to the surrounding sediment. This radial pattern is presumed to indicate the emission centres of very high fluid/mud ratio flows (mainly liquid), flowing on smooth slope deposits ranging from 1 to 5°. These features resemble piping/rill structures reported from high-density brine fluids outflowing from salt diapirs. Thus, we interpret these geomorphic

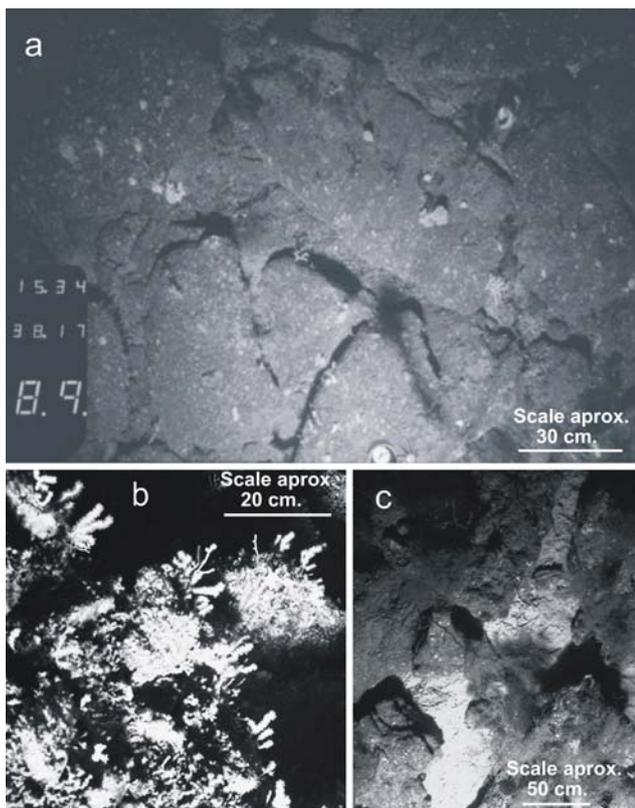


Fig. 3 **a** View of the sea floor covered with HDAC slabs, track 5. **b** Detail of cold-water corals *L. pertusa* in life position over HDAC crusts, track 3. **c** Fissure with mud ejection in HDAC crust, track 5 (see Fig. 1 for track locations)

structures as being small leakages of fluids, probably associated with high-density waters/brines from underlying diapiric structures.

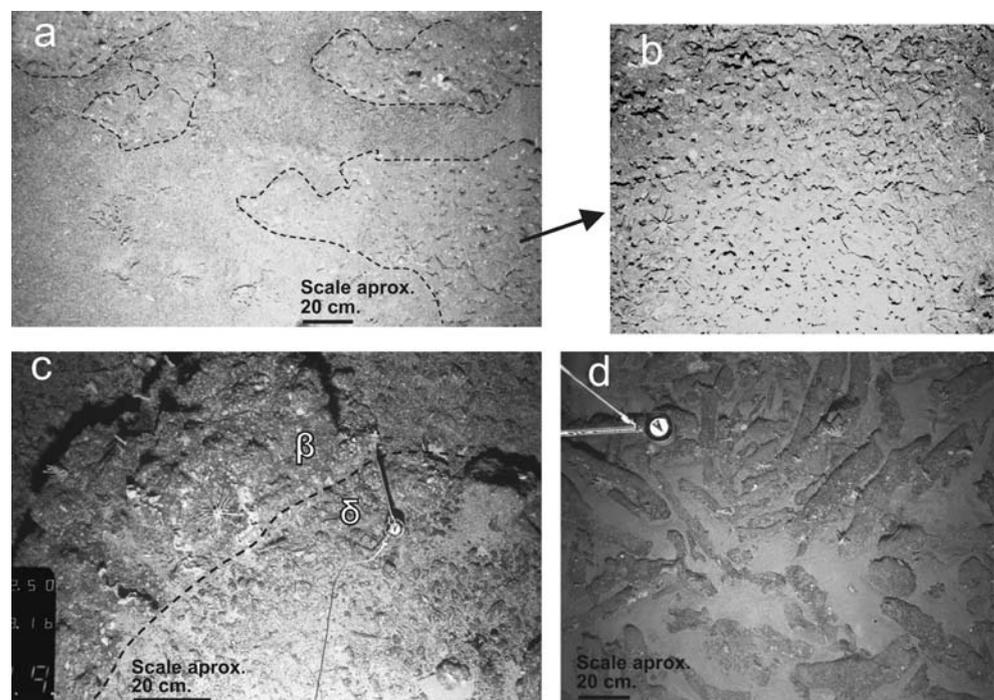
Hydrocarbon-derived authigenic carbonates: types and morphologies

Crusts, slabs and chimneys of hydrocarbon-derived authigenic carbonates (HDACs) have been found extensively in the Gulf of Cádiz (e.g. Díaz-del-Río et al. 2003). Based on analyses of underwater camera photographs from the carbonate-mud mounds (Ibérico, Cornide, Arcos, Coruña) along the Guadalquivir Diapiric Ridge, we distinguish the following types of geomorphic HDACs (Figs. 3 and 4): (1) massive crusts (“ β ” in Fig. 4c), (2) steeply dipping to vertical slabs (Fig. 3), (3) “honeycombed” carbonate crusts (Fig. 4a,b), (4) nodular aggregated crusts (“ δ ” in Fig. 4c), and (5) pipe-like formations (chimneys; Fig. 4d).

Massive crusts and slabs of HDACs have been observed over vast sectors. Most of these are colonised by sessile organisms. The dominant fauna that have been found are living deepwater corals (*L. pertusa* and *M. oculata*), large colonies of *Callogorgia verticillata*, many specimens of sea urchins, Cidaridae, and Asterinidae sea stars (Fig. 3b; Cunha et al. 2002; Kopf et al. 2004). These pavings usually show fractures (Fig. 3a) and sometimes fissures (Fig. 3c). In some cases, slabs of HDACs are steeply dipping.

“Honeycombed” carbonate crust patches have been observed in the massive carbonated crusts (Fig. 4a,b). They form irregular masses with sharp limits. Generally, the

Fig. 4 **a** Patches of “honeycombed” carbonate crust inside massive carbonate crust, track 3. **b** Detail of honeycombed carbonate crust, track 3. **c** Sharp and well-defined lateral changes from massive carbonate crust (β) to nodular aggregate crust (δ), track 3. **d** Broken pipe-like chimneys of carbonate crust protruding from muddy sediments, track 1 (see Fig. 1 for track locations)



diameter of these isolated masses is about 1 m but, locally, patches 5 m in diameter have been found. The surface texture is quite rough, with numerous sharp protuberances and subrounded concavities of 2–5 cm diameter. These textures might be due either to partial dissolution of the massive HDACs or to colonisation and boring by lithophilous organisms such as bivalves, worms, barnacles and sponges.

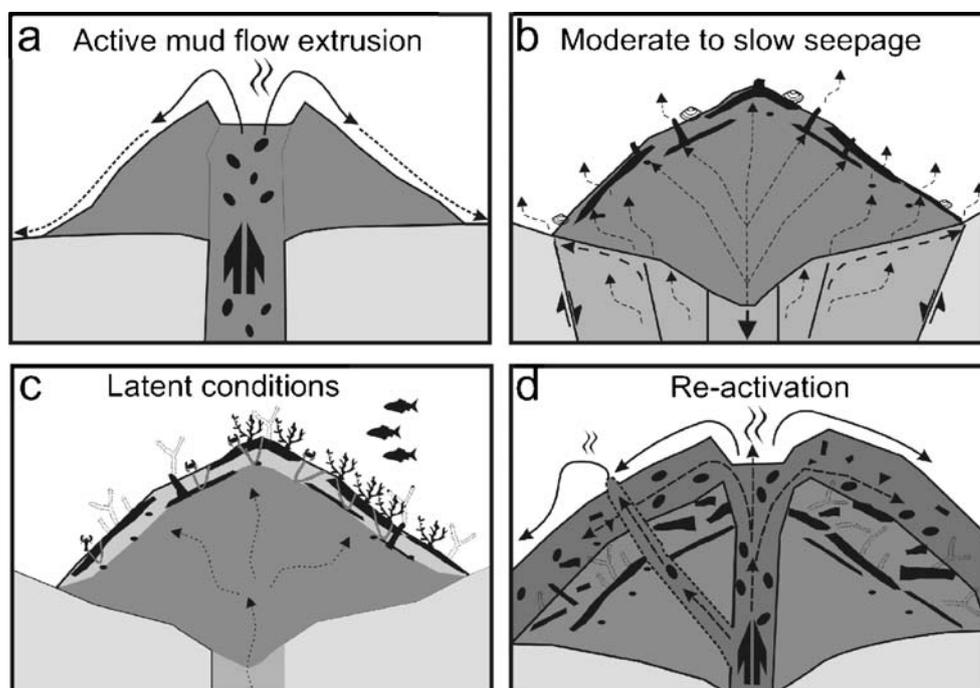
In addition, nodular aggregated crusts have been recorded on underwater photographs. Well-defined boundaries between highly colonised carbonate crusts and nodular aggregates can be observed on the Coruña mound (Fig. 4c). Along some photographic tracks, they have been documented continuously for more than 100 m. Nevertheless, it is possible to find local patches of nodular aggregated crusts of 1–2 m diameter. Nodules ranging from 1 to 20 cm are subrounded and cemented by HDACs.

The most outstanding feature of the carbonate-mud mounds is the occurrence of pipe-like chimneys, lying scattered in dense concentrations over the seabed (Fig. 4d). Although most of these lie horizontally on the sea floor, some can be found protruding from muddy sediments. Even though they do not strictly form a continuous crust, they can be considered as a paving of carbonate precipitations overlying/protruding from plastic mud deposits (Somoza et al. 2003). Some of these chimneys are longer than 3 m, with a wide range of morphological types (spiral, cylindrical, conical, mushroom-like and mounded), numerous nodular protuberances, and ramified structures (Díaz-del-Río et al. 2003). The mechanisms for the formation of these types of HDACs are still controversial. It is presumed that

distinct mechanisms are responsible for the great variety of morphologies found in this area and other nearby areas of the Gulf of Cádiz. We suggest that pipe-like chimneys are related to two main processes: the migration of hydrocarbon fluids through vertical fissures, like the vertical deep-rooted “seismic chimneys” observed on seismic images (Díaz-del-Río et al. 2003), and the saturation of hydrocarbon fluids through networks of burrows beneath the sea floor and precipitation of HDACs (Mata et al. 2005).

The majority of HDACs that constitute slabs, crusts and pipe-like chimneys show similar petrographical and mineralogical characteristics. HDACs are composed mainly of authigenic carbonates (Fe-dolomite, high-Mg calcite, and calcite), with a minor quantity of detritic minerals (quartz, zircon and clay minerals) and goethite pseudomorphing pyrite surrounded by carbonate rims of iron dolomite (Díaz-del-Río et al. 2003, Merinero et al. 2005). Aggregates of goethite after pyrite, which form framboids and framboidal aggregates, suggest sulphate-reduction bacteria-related biomineralization forming both chimneys, crusts and slabs. Iron sulphides and carbonate aggregates have been related to fermentation by sulphate-reducing bacteria (SRB) in association with methane-oxidizing archaea, probably followed by iron oxidation (Díaz-del-Río et al. 2003; Pinheiro et al. 2003; Mata et al. 2005; González et al. 2006). $\delta^{18}\text{O}$ average values of dolomite (+6‰) suggest precipitation in equilibrium with seawater at 8–9°C. $\delta^{13}\text{C}$ values ranging from –20‰ to –48‰ PDB have been interpreted as derived from the oxidation (bacterially mediated hydrocarbon oxidation) of a mixed thermogenic/biogenic gas (Díaz-del-Río et al. 2003). $^{87}\text{Sr}/^{86}\text{Sr}$ values from carbonate

Fig. 5 a–d Proposed evolutionary model for the development of mud volcanoes and carbonate-mud mounds in the Gulf of Cádiz. **a** Active mud-breccia flow extrusion and building of the cone-shaped volcanic edifice. **b** Reduced seepage activity, with collapse of the edifice and formation of extensive HDACs by chemosynthetic organisms. **c** Latent conditions: formation of hardgrounds and colonisation by non-chemosynthetic organisms such as deepwater corals (e.g. *L. pertusa*, *M. oculata*), and development of a net of burrows. **d** New episode of active mud-flow extrusion, with embedded fragments of HDACs and deepwater corals (see text for explanation)



chimney cones vary in the range 0.7087–0.7091, in agreement with the precipitation from Holocene to Recent seawater (Mata et al. 2005).

Discussion: evolutionary model

We suggest that the abovementioned widespread seep-associated carbonate-mud mounds may be a consequence of alternate periods of: active mud-flow extrusion (mud-volcano formation) (Fig. 5a), moderate to slow seepage activity with the formation of HDACs through microbially mediated anaerobic oxidation of hydrocarbons (Fig. 5b), and the development of hardgrounds and colonisation by non-chemosynthetic organisms such as deepwater corals (e.g. *L. pertusa*, *M. oculata*; Fig. 5c). Each reactivation of deep-seated fluid venting gives rise to another period of mud-breccia flow extrusion (Fig. 5d). At this stage, this mud breccia is characterised by large clasts of previously formed HDACs slabs, crusts, chimneys, etc. During this period, mud flows can extrude through secondary feeder channels developed as a consequence of the subsidence and collapse of the mud-volcano edifice (Fig. 5b).

Mud-breccia flows reflect active periods of degassing and associated mud and fluid eruption. They are considered to be catastrophic events interspersed with periods of inactivity (e.g. Guliyev and Feizullayev 1997). The morphology of mud volcanoes has been related to extrusion characteristics such as the reactivation period, width of the feeder channel, and shear strength of mud-breccia extrusion (Dimitrov 2002). The connection between extrusion characteristics and morphology has been observed in the Mediterranean Ridge and Black Sea (Camerlenghi et al. 1995). Therefore, conical mud volcanoes have been related to inactive/poorly active fluid flows with narrow feeder channels, whereas flat-topped mud volcanoes have been related mostly to more active fluid flows with shorter reactivation periods, wider feeder channels, and the extrusion of mud with lower shear strengths (Ivanov et al. 1996; Lykousis et al. 2004). In the Caspian Sea, most mud volcanoes are related to deep regional fault systems, suggesting that mud-volcano formation is due to instantaneous pressure release events through diatremes (Yusifov and Rabinowitz 2004).

Activity of small seeps in some of the mud volcanoes surveyed in the Gulf of Cádiz is inferred from the presence of scattered patches of chemosynthetic fauna such as *Pogonophora* sp. and *Calyptogena* sp. (Pinheiro et al. 2003; Kopf et al. 2004). In addition, in mud-volcano complexes composed of multiple cones, it has been observed that there are differences in the sea-floor products and geomorphic features along the cones. Thus, the Hespérides mud-volcano complex revealed the presence of abundant HDAC crusts and slabs on the older cones,

whereas the younger ones showed only evidence of mud flows over their surface with the absence of carbonates (Kopf et al. 2004). Methane concentration values obtained from the Hespérides mud-volcano cones were low (<0.2 mM), probably reflecting inactivity or slow rates of fluid venting. This fact suggests partial “lithification” of mud volcanoes during slow-rate fluid-venting episodes through anaerobic oxidation of hydrocarbons. Moreover, the presence of brecciated structures in some of the carbonate samples from these mud volcanoes may also indicate repetitive eruptions interspersed with latent periods (Mata et al. 2005). These periodic blow-out processes are also imprinted in mud flows by the intercalation of different sand, mud and clay contents with a Gaussian and bimodal clastometric distribution (Martín-Puertas et al. 2003). This periodicity in mud extrusion is also evidenced on high-resolution seismic profiles, where several mud-flow deposits of mud volcanoes appear laterally intercalated with contourite units of the Mediterranean Outflow Water, producing a “Christmas-tree” seismic image (Somoza et al. 2003).

In addition, there is evidence of an evolution of the mud-breccia products ejected in mud volcanoes, from gassy mud-breccia flows to high-viscosity mud-breccia flows. In this sense, “dome-like” features with steep slopes have been identified on geophysical profiles and swath bathymetry of the central caldera of several mud volcanoes such as Anastasya, Pipoca and Almazán (León et al. 2001). We presume that these domes may be the consequence of partial lithification by HDAC products and/or produced by the ejection of the end products of viscous mud-breccia flows. This viscosity evolution can be related to variations in sediment pore pressure during periods of tectonic reactivation. Degassification caused by overpressure triggered by tectonic pulses varies from an initial “energetic” stage to final stages when tensional conditions of the sediment tend to normalize. This variation—from more to less “energetic” conditions in the pore pressure of extruding sediments—will cause changes in the viscosity of mud-breccia flows, i.e. the later the ejections, the more viscous the extruded sediment.

The evolutionary model proposed here leads to the suggestion that carbonate-mud mounds are built up by episodes of varying fluid-venting rates, from active mud-flow extrusions to moderate-slow seepage activity and, eventually, latent conditions. Mud-flow reactivation periods might be triggered by compressional tectonics. Presently, there is not enough information on the role of oceanographic factors controlling the variability in fluid rates. It has been generally accepted that high sea-level periods tend to increase shallow subsurface hydrate formation by increasing hydrostatic pressure and, consequently, producing a self-sealing of the fluid venting. However, recent models suggest that dynamic currents have much more influence on hydrate stability and thus, on sea-floor fluid

venting. In this way, for this area at the confluence between the Mediterranean Outflow Waters and Atlantic Deep Waters, it has been proposed that the influence of warmer Mediterranean Outflow Waters during glacial periods has given rise to dissociation of hydrates, thereby increasing fluid venting during lowstand sea levels (Gardner et al. 2001). Heat-flow probes from several mud volcanoes of the Gulf of Cádiz show evidence that the subseabed geothermal gradient and, therefore, the depth of hydrate stability, is influenced by the Mediterranean Outflow Waters (Kopf et al. 2004). There is no information on the timing of migration and colonisation by species of deepwater corals such as *L. pertusa* and *M. oculata* on chemosynthetic carbonate mounds. It is probable that this takes place during periods of increasing “invasions” of the warmer Mediterranean fauna in relationship with glacial-deglaciation cycles. In addition, variations in palaeoceanographic conditions may influence some dissolution processes occurring on the carbonate-mud mounds, such as in the “honeycombed” carbonate crust areas observed in chemosynthetic crusts.

Conclusions

1. Submarine photographs taken on deepwater carbonate-mud mounds located along the continental margin of the Gulf of Cádiz (eastern Central Atlantic) provide a great variety of images of hydrocarbon seep-related geomorphic features on the sea floor.
2. Recognised fluid-induced geomorphic features, at scales ranging from metres to centimetres, include both mud-breccia flows and seep precipitates, designated here generically as hydrocarbon-derived authigenic carbonates (HDACs).
3. Based on the synthesis of all the reviewed visual, geophysical, geochemical and mineralogical data, we have categorized the geomorphic seeps into the following types:
 - Mud-breccia flows and liquid seepages that can be grouped as (1) viscous and high viscous mud-breccia flows, (2) gassy mud-breccia flows, and (3) small-scale piping/rills; and
 - HDAC types including (1) massive crusts, (2) “honeycombed” carbonate crusts, (3) nodular aggregated crusts, (4) steeply dipping to vertical slabs, and (5) pipe-like formations (chimneys).
4. The abovementioned widespread features observed on carbonate-mud mounds may be a consequence of alternate periods of (1) active mud-flow extrusion (mud-volcano formation), (2) moderate to slow seepage activity, with the formation of HDACs through microbially mediated anaerobic oxidation of hydrocarbons, and (3) formation of hardgrounds and colonisation by non-chemosynthetic organisms such as deepwater corals (e.g. *L. pertusa*, *M. oculata*).
5. These evolutionary stages of hydrocarbon-related structures identified in the Gulf of Cádiz suggest that fluid-venting episodes may be modulated by tectonic and oceanographic factors in response to (1) African-Eurasian plate convergence, (2) downslope movements of salt/shale, which form compartments of pressurized hydrocarbon fluids along the continental slope, and (3) massive destabilisation of gas-hydrate deposits by episodic events of increasingly warmer Mediterranean Outflow Waters.

In terms of present-day, short-term dynamics, the location of such a large concentration of gas-related structures in the Gulf of Cádiz, adjacent to the Strait of Gibraltar, the link between the Mediterranean Sea and the Atlantic Ocean, makes this region an attractive potential field laboratory, one that calls for detailed observation and monitoring of the dynamics of methane fluxes and morphologies and associated chemosynthetic ecosystems.

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