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ORIGINAL

A comparative mineralogical study of gas-related sediments of the Gulf of Cádiz

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Abstract The Gulf of Cádiz area has been extensively surveyed in recent years and several gas-related fluid escape seafloor structures have been identified. In this study, gravity cores, collected during the ANASTASYA/00 and ANASTASYA/01 cruises, on mud volcanoes, hemipelagic sediments and dredged material from diapiric structures, have been studied. A comparative mineralogical analysis by XRD and SEM of samples from different areas has been performed in order to determine whether there is a characteristic mineralogy related to these fluid escape structures, and also to determine the origin of the mud matrix and constrain the depth of the parent units. The mineralogical analysis reflects the different origins of the different units described in the cores: hemipelagic material of the slope, clays that underlie the mud volcanoes and are discharged at the sea bottom surface, and authigenic and diagenetic minerals possibly involved in the anaerobic oxidation of methane in the mud volcano sediments. The bulk and clay mineral composition of the sediments reflects the differences between hemipelagic materials and the mud matrix. Mud volcanoes have a smectite content that could be analogous to the underlying clay-rich units that form part of the diapiric structures related to fluid escape structures. This clay mineralogy association implies a weak thermal maturation of clays, and therefore that the parent units are buried no more than a few kilometres. This mixing of clays of different origins onto the seafloor leads to a new consideration regarding the abundances and distribution of clay minerals along continental margins where deep seeping fluids occur. If adequate analysis of compositions and structure is made, then the smectite content in sediments of many mud volcanoes would be a candidate as tracer of the source of seepage fluids.

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Introduction

Submarine mud volcanoes are one of the seafloor expressions of the expulsion of argillaceous material from deeper areas, generated by an extrusion activity involving the transport of sediments, liquids and gas from deeper areas to the seafloor (Milkov 2000; Kopf 2002 and references therein). Sediments of a mud volcano, mud flows, are made of mud and clasts carried up from deeper areas associated with the fluids. Authigenic minerals, resulting from the anaerobic oxidation of methane in the discharge areas, may also be present in the mineral assemblage of the resulting sediments. Transformation of all these minerals can give rise to a new generation of diagenetic minerals that can mask the characteristic mineralogy of the pristine sediments at the methane-venting system. Authigenic and diagenetic carbonates in methane-active areas have been the subject of many studies because they form when methane is oxidized in contact with sulphate and in association with microbial communities (Hinrichs et al. 1999; Boetius et al. 2000; Michaelis et al. 2002).

Although mineralogic and geochemical studies related to microbial activity and fluids have been addressed in the last decade, the study of the origin of the mud breccia or the diagenetic changes of these sediments has not been so intensely investigated. Regarding the origin of the mud flow, both the matrix and the clasts have to be taken into consideration. The petrography of the clasts and micro-palaeontogical studies of both mud and clasts are the main methods used to study the origin and depth of the mud flow (Akhmanov 1996; Kopf et al. 2000; Ovsyannikov et al. 2003; Pinheiro et al. 2003). The expelled materials act as a tectonic window of underlying strata and the nature of both components, clasts and matrix, providing important information about the deeper units, when comparing with the regional geology (Cita et al. 1981; Robertson and Kopf 1998; Ovsyannikov et al. 2003; Pinheiro et al. 2003).

The study of clay mineralogy in fluid-rich environments, such as cold seeps and mud volcanoes, can be important for several reasons.

1. Clay dehydration at depth can generate fluids and overpressures like those found in accretionary complexes (Colten-Bradley 1987; Ramsom and Helgeson 1995; Kastner et al. 1995; Underwood and Deng 1997; Deng and Underwood 2001; Brown et al. 2001, 2003; Kopf et al. 2001).
2. As a consequence of the transformation of hydrated clays, the crystallochemical characterisation of illite, chlorite or other interlayered clay minerals can be an indicator of depth, if a reliable temperature gradient is available (for recent reviews, see Merriman and Frey 1999, and Merriman and Peacor 1999).
3. Similarly, a study of the detailed structure and composition of the new phyllosilicates can provide important information about the nature of the fluids (Alt 1999). The boron geochemistry of clays has been used in accretionary complexes as a tracer to estimate the depth of the fluids and the mud mobilization below ground (Kopf and Deyhle 2002; Teichert et al. 2005).
4. Experimental studies demonstrate that a clay-gas hydrate compound is possible. The structure of K and Na montmorillonite clay and the assimilation of methane have been studied by Gist (2000), Titiloye and Skipper (2000, 2005), Park and Sposito (2003), and Guggenheim and van der Groos (2003). Swelling clays such as montmorillonite can host methane hydrate in the 2:1 interlayer. The experimental work of these authors indicates that clays intercalated with gas hydrate may be a new sink for oceanic methane.

In many mud volcano sediments, a systematic increase in smectite minerals or unusual abundances compared with average regional values have been observed (Barbados accretionary wedge, the Anaximander Mountains and the Gulf of Cádiz; Kerr et al. 1970; Jurado-Rodríguez and Martínez-Ruiz 1998; Robertson and Kopf 1998; Lance et al. 1998; Zitter 2004; Martín Puertas 2004; Martín Puertas et al. 2004). These earlier data and the experimental work of Guggenheim and van der Groos (2003), showing the close relation of clays and methane at the reticular scale, suggest that the study of clay minerals in active or recent methane seep areas is necessary in order to better understand the stability field of this new compound.

In this work, a comparative mineralogical analysis of samples from gravity cores from different locations and structures in the Gulf of Cádiz has been performed in order to investigate if a characteristic mineralogy, related to the methane fluid seeping system, is found. In order to determine the origin of the matrix of the mud breccia and the depth of the source of parent units, the clay mineral content of cores has been characterised, and a preliminary interpretation about their origin is presented.

Materials and methods

The Gulf of Cádiz area has been extensively surveyed previously using different geophysical methods, and several methane gas-related seafloor structures have been identified, including mud volcanoes, areas of carbonate crusts and chimneys, gas pipes and mud mounds (Baraza and Ercilla 1996; Gardner 2001; Kenyon et al. 2001; Somoza et al. 2002; Díaz del Río et al. 2003; Casas et al. 2003; Pinheiro et al. 2003; Somoza et al. 2003; Medialdea et al. 2004; Depreiter et al. 2005; Van Rensbergen et al. 2005a, b; León et al. 2006, 2007; Fernández-Puga et al. 2007).

Gravity cores were collected during the ANASTASYA/00 and ANASTASYA/01 cruises on mud volcanoes and other gas-related structures (Fig. 1, Table 1). Cores from hemipelagic sediments and dredged material from outcropping diapiric structures (Fernández-Puga et al. 2007) have also been sampled. Table 1 shows the location and description of the gravity cores and dredged samples of this study. Mud volcanoes are from two different areas: Anastasya, Pipoca and Gades are on the Guadalquivir Diapiric Ridge Province (GDR), and Almazán and Faro are in the Tasyo field (Tasyo). Gravity cores Grifón I, II and Tachuela correspond to hemipelagic material and have been considered as the reference material in order to compare the mineralogy with that of the mud breccia. Dredged series samples labelled DA06, DA19 and DA16 (Fig. 1, Table 1) coming from clayed and marly outcrops, most likely Miocene in age (Maldonado et al. 1999), have been also studied.

Mineralogical analysis, X-ray powder diffraction (XRD) on bulk samples and <20 and <2 μm fractions, has been

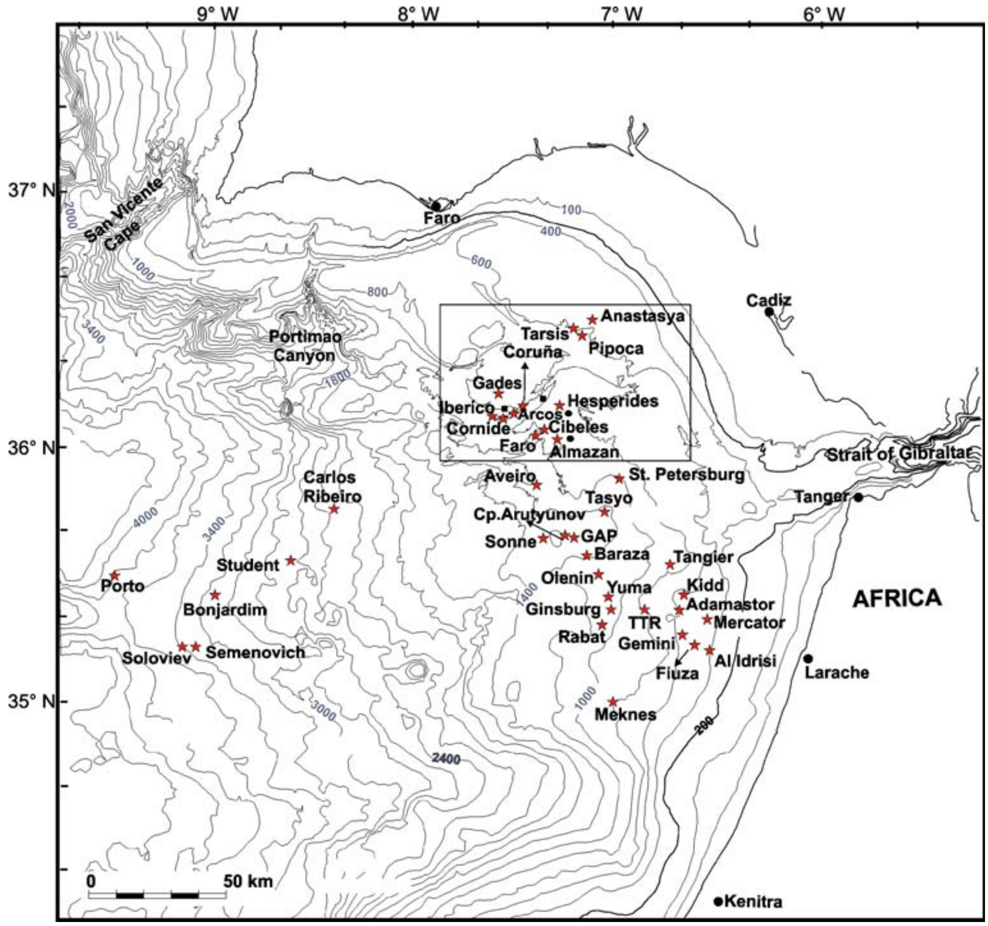


Fig. 1 Location of the mud volcanoes of the Gulf of Cádiz and the study area (after León et al. 2006). *Stars* Mud volcanoes, *circles* hemipelagic cores, *squares* dredged series (DA19/DA16/DA06)

undertaken in order to identify the constituent minerals of the sediments. Numbers of study samples are: 89 for the gravity cores of mud volcanoes (including sandy and intercalated hemipelagic samples), 37 for the hemipelagic material of Grifón I, II and Tachuela, and six samples from the dredged outcrops. On the basis of the results of the bulk mineralogical and its variability, a group of samples was selected in order to determine clay mineralogy (Table 1). Suspensions of <20 and <2 μm fractions were separated by centrifuge. Oriented aggregates of <20 and <2 μm sizes over glass slides were analyzed by means of XRD on air-dried, glycolated and heated samples (Moore and Reynolds 1997). Scanning electron microscopy and EDS analyses were performed with the FEI-Quanta ESEM of the University of Cádiz in carbon-coated dried sediments in order to obtain both the morphologies and the chemical composition of the detrital and authigenic minerals.

Results

Figure 2a,b shows representative cores of mud volcanoes from the two study areas and a gravity core corresponding to hemipelagic sediments (Tachuela, Fig. 2c). Cores recovered from the GDR and Tasyo fields (50–250 cm) are made of mud and mud breccia with intercalated hemipelagic sediments. Selected cores (Almazán from the Tasyo field, and Gades from the GDR province) are shown in Fig. 2a,b. All the study cores related to seeping gas have a brownish sandy layer (up to 15 cm) at the top of the sequence. The characteristic colours of the mud breccia are green to dark grey. A strong smell of H_2S was observed during sampling. Liquefaction features, probable due to a fast dissociation of hydrates, and the occurrence of chemosynthetic fauna (*Pogonophora* tubeworms) were also documented (Gardner 2001; Kenyon et al. 2001; Pinheiro et al. 2003; Stadnitskaia et al. 2006). Almazán and Faro are composed mainly of mud breccia and an upper sandy layer but Anastasya, Pipoca and Gades (from GDR province) have hemipelagic intercalated units (Martín Puertas et al. 2007).

The main minerals of the mud breccia of the GDR field area (Fig. 2b) are: quartz (10–55%), phyllosilicates (15–45%), and carbonates, calcite and dolomite (up to 50%). Feldspars and pyrite also occur as minor phases (<5%), and sometimes they were detectable only during SEM study. Figure 2b shows the distribution of the main minerals in the Gades gravity core that comprises a thick unit (up to

Table 1 Data of gravity cores and dredged studied samples of this study (after Somoza et al. 2003; *n* number of study samples/number of samples in which clay mineralogy has been determined)

Volcano label	Water depth (m)	Recovery (cm)	Location (lat., long.)		Sedimentary units
Anastasya (GDR) ANAS01-TG02	452	75	36°3′ 19.10″	07°09′ 05.87″	Sandy layer at top (5 cm), mud breccia unit with heterometric clasts and hemipelagic sediments at bottom (*n*=15)
Pipoca (GDR) ANAS01-TG01	536	250	36°27′ 37.07″	07°14′ 44.57″	Sandy layer at top and intercalated mud breccia and hemipelagic units (*n*=24/7)
Gades (SDG) ANAS01-TG04	915	265	36°14′ 09.90″	07°37′ 00.24″	Sandy layer at top, and dark green mud breccia (*n*=16/7)
Almazán (Tasyo) ANAS01-TG08	830	106	36°03′ 03.89″	07°20′ 03.31″	Sandy layer and mud breccia with an intercalated unit of hemipelagic sediments (10 cm, *n*=20/6)
Faro (Tasyo) ANAS01-TG14	795	60	36°04′ 03.91″	07°26′ 18.29″	Sandy layer and mud breccia unit (*n*=14/3)
Grifón I, ANAS01-TG09	843	238	36°06′ 4.20″	07°18′ 43.80″	Hemipelagic sediments (reference sediments, *n*=10/3)
Grifón II, ANAS01-TG10	851	218	36°05′ 53.40″	07°19′ 32.40″	Hemipelagic sediments (reference sediments, *n*=10/3)
Tachuela, ANAS01-TG17	912	243	36°10′ 28.80″	07°24′ 37.80″	Hemipelagic sediments (reference sediments, *n*=17/3)
DA-6 (dredged)	721	–	36°11′ 11.40″	07°19′ 24.60″	Blue marls (*n*=2/2)
DA-16 (dredged)	874	–	36°10′ 10.20″	07°33′ 00″	Blue marls (*n*=2/2)
DA-19 (dredged)	850	–	36°09′ 15.00″	07°33′ 23.40″	Blue marls (*n*=2/2)

265 cm) of dark mud in which no clasts were detected. Dolomite and calcite are frequent, while aragonite is not present. Dolomite can vary from 5 to 50% over distances as short as 15 cm (195–180 cm depth in Gades core), and this variation is not related to changes in sediment type.

SEM images (Fig. 3) show pyrite as euhedral crystals that occur both in framboids and in irregular groups in the matrix (Fig. 3a). There is a range of pyrite crystal sizes, which can be up to several mm across. Calcite is frequent as a biogenic component, coccoliths being abundant (Fig. 3b,d), but it also is present as micron-sized, rounded rhomboidal crystals. Glendonite, representing calcite pseudomorphs after probable ikaite, have been observed (Fig. 3c). This aggregate shows typical radial bi-pyramidal crystals. The fine-grained mud matrix shows abundant euhedral dolomite crystals up to 15 μm in length (Fig. 3d) in a fine-grained clayed matrix.

The clay mineralogy of the <20 and <2 μm fractions of all the samples is characterised by illite, chlorite, kaolinite and smectite. The most abundant clay mineral is illite (average value 50%). The smectite content is higher at the top of the sequence in the Gades gravity core, reaching up to 25 and 21% at 46 and 36 cm depth respectively. Clay minerals show characteristic shapes such as wavy and curly layers under the SEM (Fig. 3b,d). The EDS analysis of the clay minerals of the mud matrix shows dioctahedral compositions (Al) for illite and smectite.

The mineralogy of Tasyo mud matrix samples is similar to that of the GDR samples but the relative percentages of the various minerals are different. In Fig. 2a, the mineralogy of the bulk samples and the clay fraction can be seen for the Almazán mud volcano. In the mud breccia units (15–65 and 75–115 cm depth), clay minerals can be abundant (60%) in bulk samples, and smectite is present in considerable quantities in the clay fraction (23% average value). In the hemipelagic unit of the Almazán mud volcano (70 cm depth), quartz and calcite increase and clay minerals are not so abundant. The dolomite content also is greater in the mud breccia units than in the hemipelagic or sandy units. For the Faro mud volcano samples, clay mineral percentages range from 45 to 90%; these samples have the same smectitic content as those from Almazán (23% on average). In the Almazán and Faro mud volcano mud breccia, the dolomite crystals can be imaged easily at the SEM scale as micron-sized euhedral crystals up to 15 μm long (Fig. 4a–d). Also, 1–2 μm smectite crystals are omnipresent, showing a clear Al-rich chemical composition, as determined by EDS analysis. As in the GDR area, pyrite crystals are common (Fig. 4e). Other minor phases determined by SEM study include micron-sized euhedral albite crystals, phosphates and euhedral 2-μm calcite crystals (Fig. 4c).

Hemipelagic sediments, (Grifón I, II and Tachuela) are homogeneous, structureless, green to dark grey, with

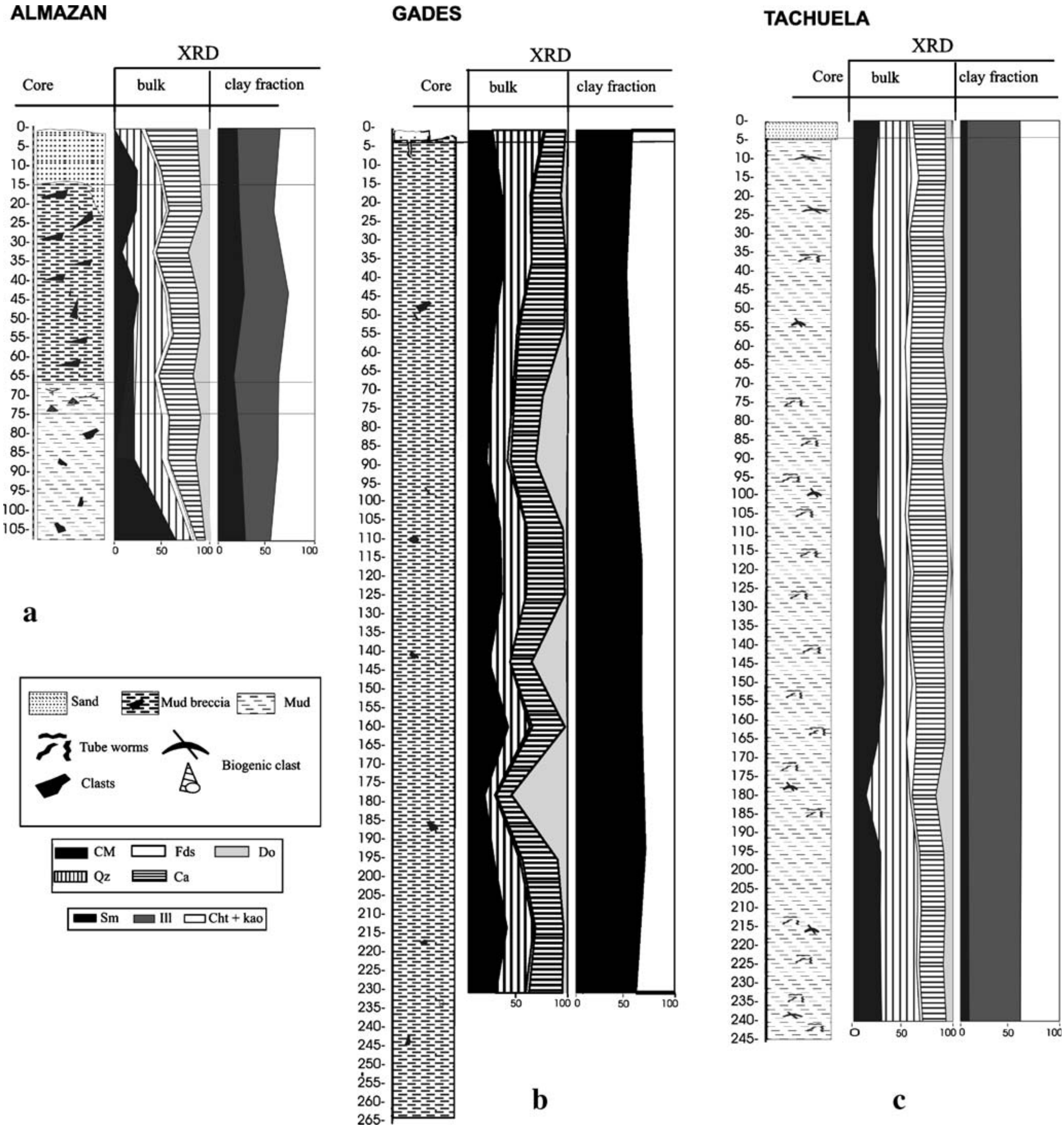


Fig. 2 **a**–**c** Representative gravity cores from the GDR, Tasyo areas (**a**, **b**) and hemipelagic sediments (**c**). **a** Anas01-TG08: Almazán mud volcano gravity core; **b** Anas01-TG04: Gades mud volcano gravity core; **c** Anas01-TG17: Tachuela gravity core (hemipelagic)

biogenic clasts and evidence of burrowing activity. Figure 2c shows the mineralogy of the sediments from Tachuela. The mineralogy of the three study cores shows no significant differences between the base and the top. Figure 5a show representative XRD patterns of three study samples from hemipelagic cores (TG-09/TG-10 and TG/17). The main differences between these three patterns are the ratio of quartz to calcite. Regarding the clay minerals, smectite is less than 5% and illite is most abundant (50%; Fig. 2c). Chlorite and kaolinite are also present (35–40%). Most of the samples from hemipelagic sediments show similar mineralogy and clay mineralogy. SEM images (Fig. 6d,e) show abundant detrital grains of calcite, quartz, biogenic clasts (coccoliths and foraminifers) and fine-grained clay minerals.

The six dredged samples (series DA06/DA16/DA19) showed an intense blue colour when they were wet.

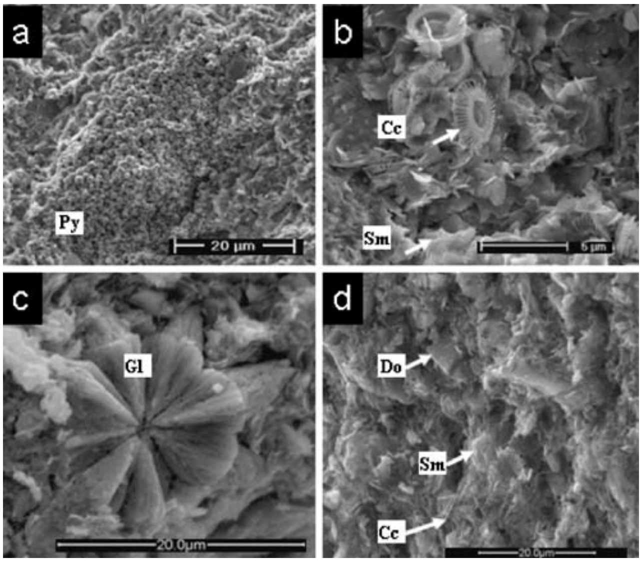
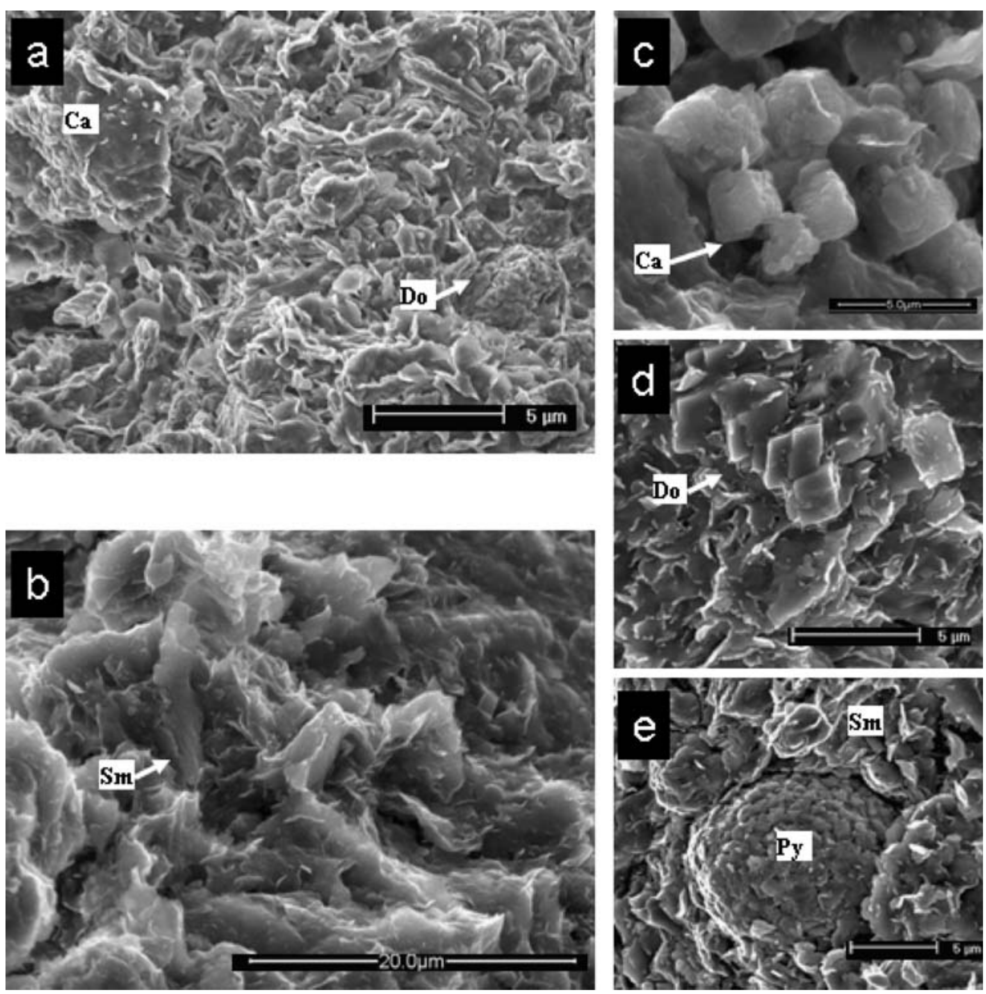


Fig. 3 **a**–**d** Representative SEM images of the Gades gravity core. **a** Pyrite crystals (*Py*) in the clayey matrix; **b** matrix made of coccoliths (*Cc*) and clays (*Sm*); **c** glendonite pseudomorphs after ikaite (*Gl*); **d** fine-grained matrix with smectite (*Sm*) and dolomite (*Do*)

Underwater imagery showed spectacular outcrops of plastic-like materials with carbonate concretions (chimneys) emerging from the outcrop (León et al. 2006, 2007). XRD analyses of dredged samples show a mineralogy in which clay minerals and carbonates are the principal components (Table 2, Fig. 5b,c). The clay minerals can comprise up to 84% of the bulk samples; therefore, the dredged samples can be considered as coming from a very clay-rich outcrop with a variable carbonate content. The smectite content of the clay fraction is very high (Fig. 5c), up to 62% of the clay fraction for DA-19 samples to 20% for DA-16 samples. Figure 5b,c shows representative XRD patterns for the three dredged series and an oriented aggregate XRD pattern for a DA-19 sample where smectite is the main clay mineral. SEM images (Fig. 6a–c) show a microtexture where coccoliths are ubiquitous and micron-sized clay plates can be observed. Euhedral dolomite crystals of up to 10 µm are also present and resemble those of the mud volcanoes samples.

Figure 7 shows comparative average values of the mineralogy of the three types of samples studies, for both

Fig. 4 **a**–**e** Representative SEM images of Tasyo gravity cores. **a** Fine-grained matrix with calcite (*Ca*) and dolomite (*Do*); **b** fine-grained clay matrix made of smectite (*Sm*); **c** micron-sized rhombohedral calcite crystals; **d** micron-sized dolomite crystals (*Do*); **e** pyrite framboid (*Py*) in a clay matrix made of smectite (*Sm*)



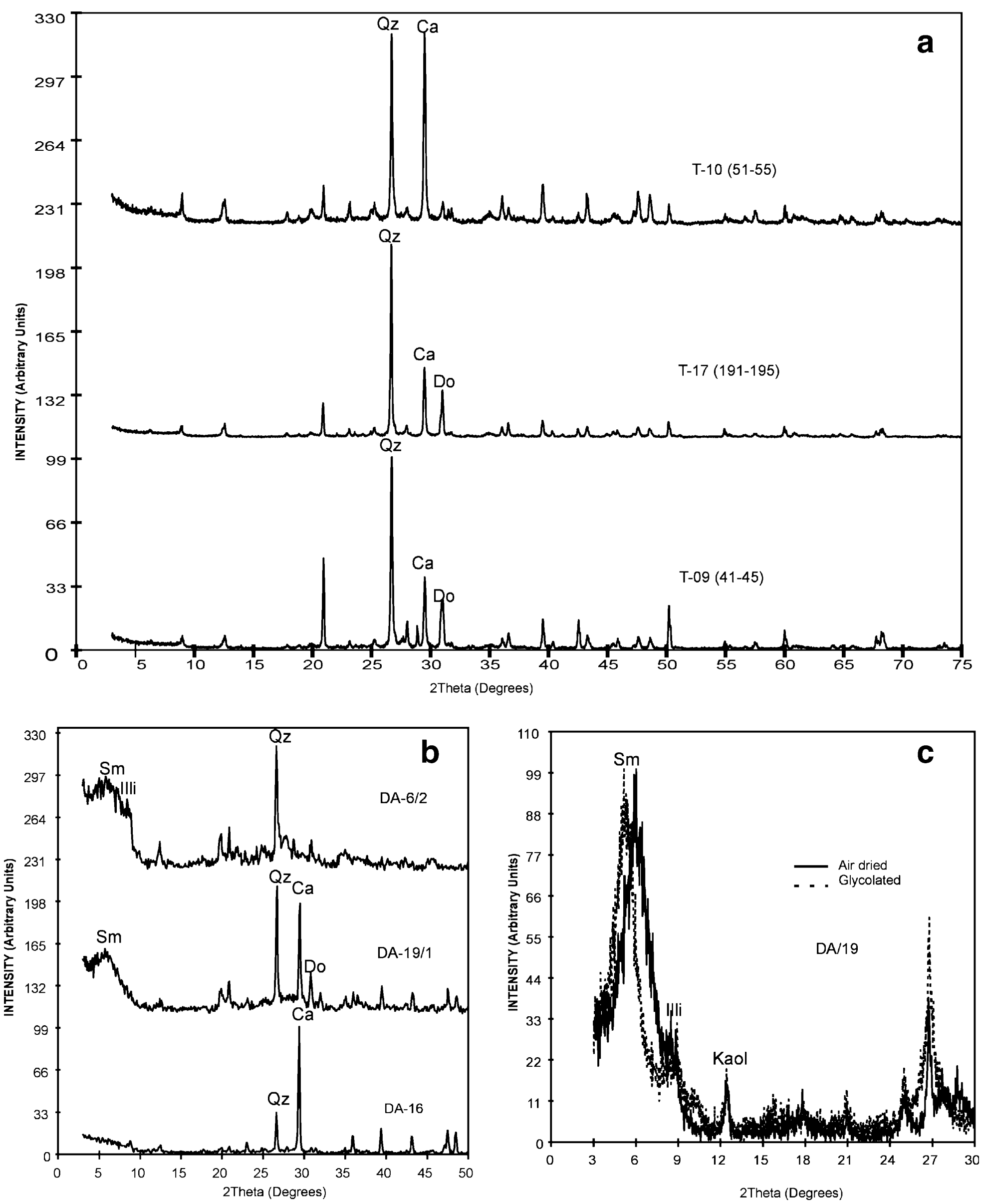


Fig. 5 **a**–**c** XRD patterns. **a** Comparative XRD patterns of representative hemipelagic samples from gravity cores: Grifón I (Anas01-TG09), Tachuela (Anas01-TG17) and Grifón II (Anas01-TG10). *Qz* Quartz, *Ca* calcite, *Do* dolomite. **b** Comparative XRD patterns from DA series (dredged outcrops). **c** XRD patterns of oriented aggregates (<2 μm fraction) of a DA/19 air-dried and glycolated (*dashed*) sample. The pattern shows smectite as the main clay mineral

bulk and clay fractions: the mud breccia of GDR and Tasyo, hemipelagic sediments, and DA series (dredged samples). The main differences between all study samples are the relative percentages of the clay minerals in the bulk samples, the dolomite content, and the different type of clays in the <2 μm fraction samples. The mud breccia and dredged samples show almost similar clay mineral contents, the average dolomite content being slightly higher in the mud breccia samples than in DA samples. For the clay mineralogy analysis, smectite contents can be up to 40% of the total clay content for DA samples, the smectite also being abundant in the mud breccia but less common in the hemipelagic sediments. In general, average mineralogical values of mud breccia samples show relative percentages between those of the DA series and the hemipelagic sediments. Figure 7c shows representative XRD patterns of bulk samples with variable smectite content. Granulometric analysis also showed differences between the three types of samples (mud breccia, hemipelagic sediments, and dredged material), suggesting that they were derived by different processes and from different origins (Martín Puertas 2004; Martín Puertas et al. 2007).

Discussion

The mineralogical data from this study allow us to suggest the probable origin or provenance of the matrix of the mud breccia, and the nature of the sediments that can be found at mud volcanoes in the Gulf of Cádiz. XRD-based mineral abundances of gravity cores and dredged samples show different values for the hemipelagic sediments (Tachuela,

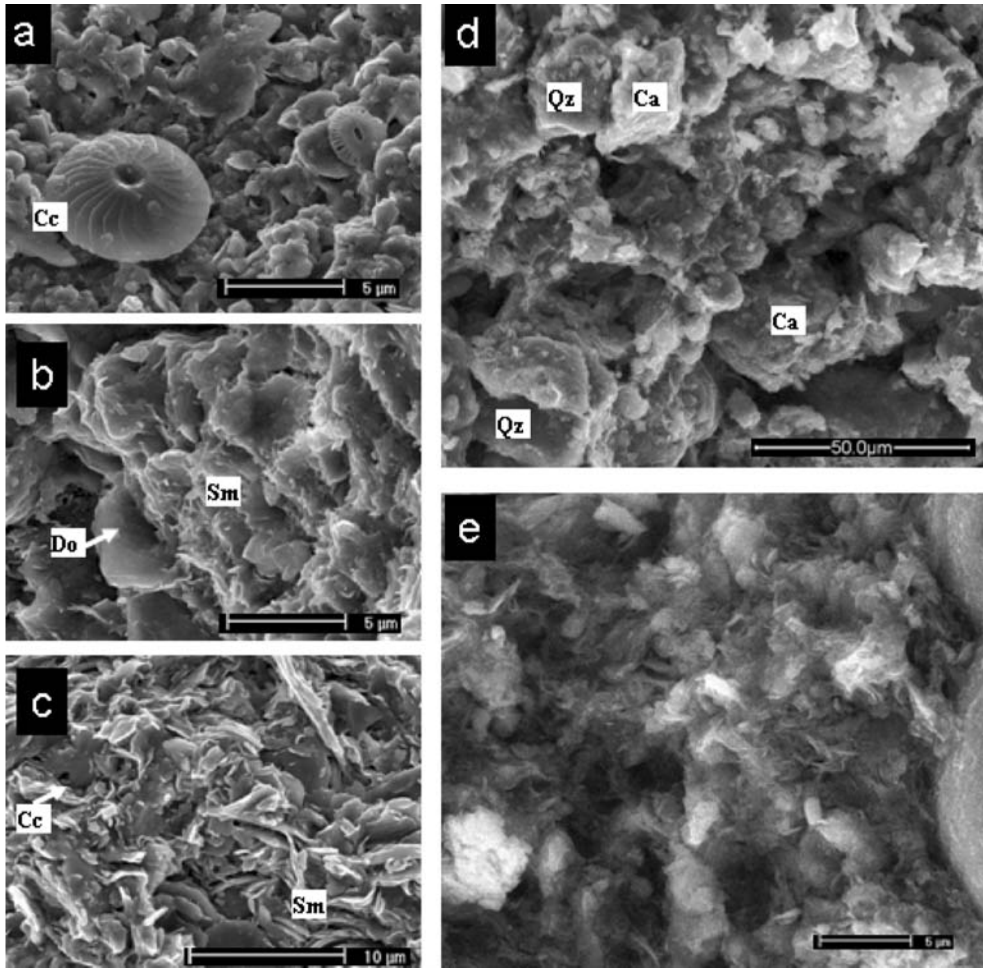


Fig. 6 **a**–**e** Representative SEM images of dredged and hemipelagic samples. **a**–**c** DA series samples showing a clay-rich matrix with smectite (*Sm*), dolomite (*Do*) and coccoliths (*Cc*). **d**, **e** Hemipelagic samples showing clear detrital grains: quartz (*Qz*), calcite (*Ca*) and clays

Grifón I, II), the DA series, and the matrix of the mud breccia (GDR-Tasyo). Differences between these samples are the amount of clays in the bulk samples (Fig. 7a), and the amount of different clays in the clay fractions (Fig. 7b). These differences in the samples confirm that the mineralogy of the components of the matrix of the mud breccia from GDR and Tasyo samples is characteristic, and has different sources to that of the hemipelagic samples. As expected, the origin of the mineralogy and clay mineralogy of the mud matrix cannot be satisfactorily explained by the fluvial or seafloor transport processes of this area at present. It has been claimed that climatic control on the transport and deposition of different clay mineral assemblages explains the differences and present distribution of clay minerals at the seafloor (Biscaye 1965; Chamley et al. 1978; Chamley 1997; Thiry 2000). Well-developed smectitic soils in present landscapes are restricted to moderate dry tropical climates as in some parts of Africa. In the Gulf of Cádiz, fluid seepage "mixes" a clay mineralogy similar to that generally found in dry to tropical areas with a mineralogy resulting from present climatic conditions and sedimentary processes in the Gulf of Cádiz. The clay distribution of continental shelf sediments has also been well characterised (Gutiérrez-Mas et al. 1996, 1997), and shows contrasting values compared with the mud matrix of breccia samples from the slope; the smectite content of shelf sediments is always less than 5% (Gutiérrez-Mas et al. 1996, 1997). Therefore, for a particular area such as the Gulf of Cádiz, an anomalous content of smectite in recent marine sediments, relative to other clay minerals such as illite, chlorite or kaolinite, may be used as an indicator of gas-rich mud extrusion related to mud volcanism/diapirism towards the surface.

Table 2 Average XRD mineralogy of dredged DA series samples (*n* number of samples, *CM* clay minerals, *Qz+Fd* quartz and feldspars, *Do* dolomite, *Ca* calcite)

	CM	Qz+Fd	Do	Ca
DA-6 (*n*=2)	84	9	<5	5
DA-16 (*n*=2)	26	9	<5	63
DA-19 (*n*=2)	54	24	<5	18

Source units or parent bed of matrix of the mud breccia

The underlying units that are mobilized at depth to generate the matrix of the mud breccia have been indirectly studied

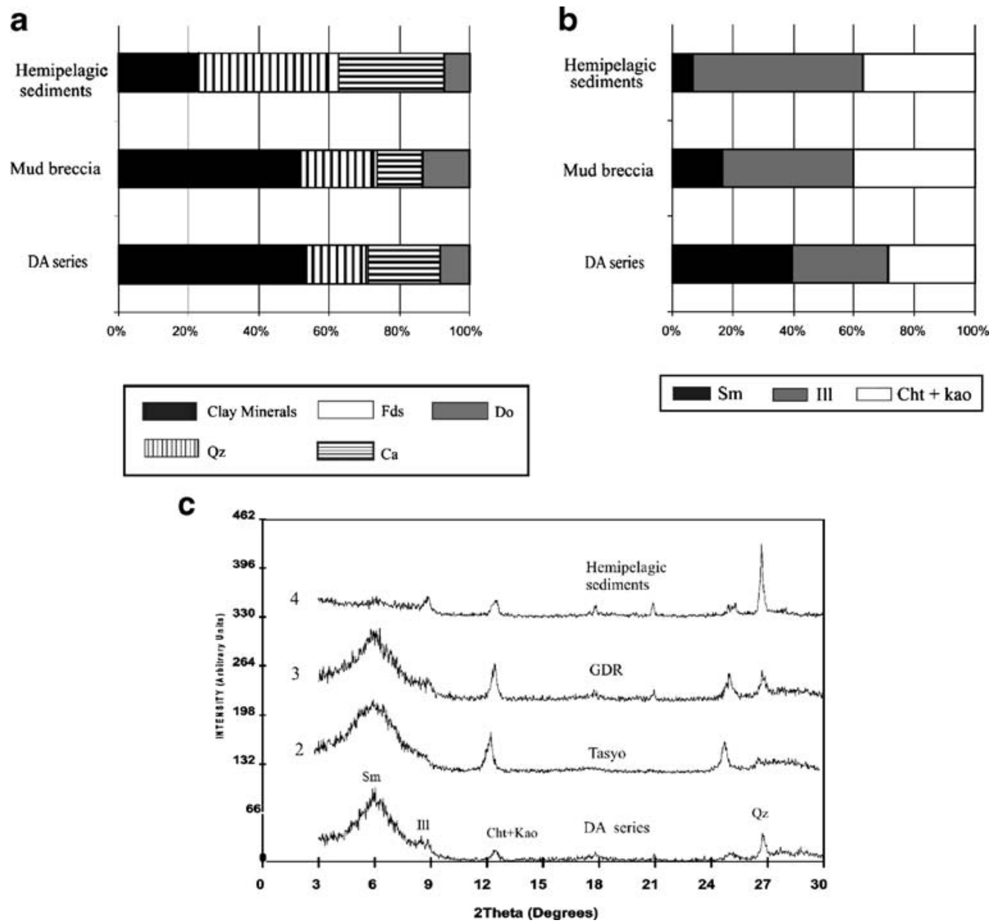


Fig. 7 a–c Comparative mineral data of hemipelagic sediments, mud breccia and the DA series. **a** Average percentages of mineralogy of bulk samples. **b** Average percentages of clay minerals from clay fractions. **c** Representative oriented aggregate patterns (air-dried) of the three different types of samples studied (dredged, mub breccia and hemipelagic)

by means of petrographic analyses of the clasts incorporated in the mud breccia, or by micropalaeontological studies of both the clast and the mud. For Mediterranean mud volcanoes, several studies of the petrography of clasts, vitrinite reflectance data, mineralogy and micropalaeontology have proposed different sources and depths (Akhmanov 1996; Premoli-Silva et al. 1996; Akhmanov and Woodside 1998; Jurado-Rodríguez and Martínez-Ruiz 1998; Robertson and Kopf 1998). A study using thermal maturation of organic material in the mud breccia of the Napoli mud volcano indicated that an important part of the mud matrix was derived from a lacustrine or riverine sedimentary unit in the subsurface, possibly from the Messinian stage (Schulz et al. 1997). Schulz et al. (1997) also calculated, considering a geothermal gradient for the zone, that the depth of mobilization ranges from 4,900 to 7,500 m. Pinheiro et al. (2003) made a micropalaeontological study of cores, coccoliths and foraminifers of several mud volcanoes in the Gulf of Cádiz (Bonjardim, Carlos Ribeiro, Jesus Baraza, Rabat, Ginsburg and Tasyo). Miocene to Pliocene species were the most common but ages up to the Upper Cretaceous were obtained. Ovsyannikov et al. (2003) studied more than 200 clasts of mud breccia extruded by the Yuma mud volcano in the Moroccan sector of the Gulf of Cádiz. They found clasts at least as old as Eocene. A clayey Miocene (Aquitanian-Burdigalian) succession was present. They also found carbonates from Langhian and Tortonian times. Before this study, however, no clay mineralogical studies of the matrix of mud breccia from the mud volcanoes of the Gulf of Cádiz had yet been published.

In this study, clay mineralogy indicates an increase in smectite relative to reference materials, suggesting a similar source of underlying materials for the different extrusions for each mud volcano in the GDR and Tasyo fields. Nevertheless, the clay association show differences between the two studied areas: for the Anastasya-Gades-Pipoca (GDR) mud volcanoes, the clay association is illite-rich whilst for the Tasyo Field, smectite is profuse. The comparative study reveals that the content and type of clay minerals in the mud matrix are more similar to the clay-rich Miocene units that outcrop on the Fila de Hormigas ridge than to any other sediments in the Gulf of Cádiz. These outcropping materials are extraordinarily clay-rich. According to Fernández-Puga (2004), Fernández-Puga et al. (2004a, b), and Fernández-Puga et al. (unpublished data), diapirs seem to play an important role in the seepage of methane and in the Neogene-Quaternary tectonics of the region. These results confirm that one of the source units than can give rise to the matrix of the mud breccia can be similar to the clayey Miocene units, diapirs and outcropping diapirs described by Fernández-Puga et al. (2004a, b). As Ovsyannikov et al. (2003) and Pinheiro et al. (2003) already suggested based on clast lithology and micropalaeontological data, Miocene formations can be present in the mud breccia of nearby areas. Miocene deposits have been described as occurring in the olistostromic units and show clayey and sandy units (Maldonado et al. 1999). It has been proposed that these can also contain gas (Riaza and Martínez del Olmo 1996; Maldonado et al. 1999). It seems that fluids will carry away softer and lighter underlying material, clayey units, rather than consolidated material, so that expelled mud would be clay-rich (Kopf 2002). Nevertheless, in this study there are differences regarding the Tasyo and GDR fields. The Tasyo samples seem to have a stronger contribution from the underlying clay units than do the GDR samples. There are at least three possibilities to explain these differences: (1) for the GDR area, smectite-rich diapirs are not in close proximity to the fluid migration pathways; (2) the clayey diapirs are much deeper in the GDR field than in the Tasyo field, and therefore clay evolution is different and the smectite has evolved into an interlayering of illite and smectite; and (3) there has been a mixture between underlying units (smectite-rich, illite-rich) as the fluid is rising, and a clear contribution of illite-rich formations to the smectite-rich mud diapirs has taken place. All the options suggested are compatible with different origins and depths of fluids, as the origin of the methane-rich fluids and the fine-grained matrix can be different.

The proposed origin of the mud breccia of Mediterranean mud volcanoes is similar to that suggested in this study for the matrix of the mud breccia of the Gulf of Cádiz Mud Volcano. Jurado-Rodríguez and Martínez-Ruiz (1998), and Zitter (2004) studied clays from Mediterranean mud volcanoes and found a clay-rich mud matrix composed of Al-rich smectite (beidellite). They proposed that the Messinian formations were the parent material. In Mediterranean Messinian sediments, there is an almost systematic increase of smectite that formed abundantly in soils developed under a temperate-subarid climate in the Mediterranean Sea region (Chamley and Robert 1980). In early Palaeogene units, smectite is abundant but it disappears upwards. This clay mineral developed on peri-Atlantic landmasses, especially in coastal plains. Source materials for the Gulf of Cádiz and the Mediterranean mud matrix may have a similar origin. Both are smectite-rich, and the smectite seems to be detrital and beidellitic (Al-rich); in addition, both areas have similar Palaeogene units underneath, developed under similar climatic conditions. For both locations, a detailed diagenetic evolution should be taken into consideration when deducing the depth from which these source materials are being transported. If a normal prograding sequence (average geothermal gradient of 25–30°/km) is considered in the Gulf of Cádiz, then the source materials should be located at a maximum depth of 3 km (Merriman and Peacor 1999 and references therein). This means that if a prograding diagenetic sequence (burial sequence) is considered below the mud volcanoes, then the mineralogy of the mud matrix would indicate a clay source that did not undergo diagenesis for the Almazán and Faro mud volcanoes, and deep diagenesis for Anastasya, Gades and Pipoca. If a reliable geothermal gradient could be obtained, a more precise maximum depth for the clay source could be proposed. In other words, no smectite-rich mud matrix can have an origin deeper than 3 km.

In this study, we consider as a tracer of depth only the thermal maturation of clays. Diagenetic changes due to the interaction of clays and fluids are not taken into consideration. A clear mineralogical association of dolomite and pyrite, similar to the mineralogy of the concretions (Díaz del Río et al. 2003), suggests that in the mud volcano sediments, anaerobic oxidation of methane coupled with sulphate reduction could also be present (Niemann et al. 2006; Stadnitskaia et al. 2006). The authigenic formation of carbonates is also a very common process, and calcite, dolomite and aragonite precipitate in these environments (Hinrichs et al. 1999; Boetius et al. 2000; Michaelis et al. 2002). In addition to these common carbonates, ikaite, a $CaCO_3$ hexahydrate, has been described as a stable low-temperature carbonate in marine environments and often related to methane releases (Suess et al. 1982; Larsen 1994; Schubert et al. 1997; Swainson and Hammond 2001; Greinert and Derkachev 2004). Greinert and Derkachev (2004) describe how seeping methane influences ikaite genesis and the ikaite-calcite transformation. In this study, a novel description has been made of calcite glendonite pseudomorphs after ikate in the Gades mud volcano, confirming the probable relation of this core with the seeping of gas. A more detailed study of the authigenic minerals of the mud volcanoes would be necessary to evaluate the changes of mineralogy at contact with methane and microorganisms in a mud volcano. Fluids percolating through the sediments can alter the pristine composition of clays, in a similar way to that in the ocean crust or other hydrothermal sites (Clauer et al. 1990; Alt 1999; Giorgetti et al. 2003). The features of this alteration, if any, could give us important data regarding the nature of the fluids. Finally, the results of Guggenheim and van der Groos (2003) show a new gas-hydrate phase made by a clay-methane hydrate compound. These authors showed how clay minerals interact in the lattice structure, with the gas hydrate changing the stability field. This experimental work shows that smectite became a "trap" for the hydrate at depth; more data are needed to understand the interaction of gas hydrates and clay minerals. In particular areas, such as the Mediterranean or the Gulf of Cádiz, where important fine-grained formations (such as Miocene units) are present underlying the mud volcanoes, this interaction should be investigated. An evaluation of these units as "methane-bearing clays" or clay-methane hydrate compounds at corresponding depths, and a comparison with other non-smectite clay units should be taken into account in future research.

Conclusions

Mineralogical analysis indicates that the cores of the mud volcanoes are made of minerals of different origins: the hemipelagic material of the slope, clays that underlie the mud volcanoes and are discharged onto to the seafloor, and authigenic and diagenetic minerals possibly derived from the anaerobic oxidation of methane in the mud volcano sediments.

The bulk and clay mineral composition of mud volcano sediments confirm the expected differences between the nature of the hemipelagic materials of the Gulf of Cádiz and the mud matrix. The matrix of the mud volcanoes' mud breccia has a smectite content corresponding to climatic and weathering conditions typical of the Miocene, confirming the deep origin from Miocene clay-rich units that are buried to a depth of no more than 3 km.

This mixing of clays of different origins on the seafloor leads to a new consideration of the abundances and distribution of clay minerals in marine sediments where gas seepage occurs. If adequate analyses of composition and structure are made, then the smectite of many mud volcanoes would help to constrain the source and depth of gas-rich mud extruded at the sea bottom.

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