Chemical Geology 266 (2009) 350–363

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Origin of light volatile hydrocarbon gases in mud volcano fluids, Gulf of Cadiz — Evidence for multiple sources and transport mechanisms in active sedimentary wedges

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A R T I C L E   I N F O

Article history:
Received 9 October 2008
Received in revised form 29 June 2009
Accepted 30 June 2009

Editor: R.L. Rudnick

Keywords:
Mud volcanoes
Light volatile hydrocarbon gases
Migration
Unconventional methane
Lipid biomarkers

A B S T R A C T

Widespread mud volcanism across the thick (≤14 km) seismically active sedimentary prism of the Gulf of Cadiz is driven by tectonic activity along extensive strike–slip faults and thrusts associated with the accommodation of the Africa–Eurasia convergence and building of the Arc of Gibraltar, respectively. An investigation of eleven active sites located on the Moroccan Margin and in deeper waters across the wedge showed that light volatile hydrocarbon gases vented at the mud volcanoes (MVs) have distinct, mainly thermogenic, origins. Gases of higher and lower thermal maturities are mixed at Ginsburg and Mercator MVs on the Moroccan Margin, probably because high maturity gases that are trapped beneath evaporite deposits are transported upwards at the MVs and mixed with shallower, less mature, thermogenic gases during migration. At all other sites except for the westernmost Porto MV, $\delta^{13}C$–CH_4 and $\delta^{2}H$–CH_4 values of ~−50‰ and −200‰, respectively, suggest a common origin for methane; however, the ratio of $CH_4/(C_2H_6+C_3H_8)$ varies from ~10 to >7000 between sites. Mixing of shallow biogenic and deep thermogenic gases cannot account for the observed compositions which instead result mainly from extensive migration of thermogenic gases in the deeply-buried sediments, possibly associated with biodegradation of C_{2+} homologues and secondary methane production at Captain Arutyunov and Carlos Ribeiro MVs. At the deep-water Bonjardim, Olenin and Carlos Ribeiro MVs, generation of C_{2+}-enriched gases is probably promoted by high heat flux anomalies which have been measured in the western area of the wedge. At Porto MV, gases are highly enriched in CH_4 having $\delta^{13}C$–CH_4~−50‰, as at most sites, but markedly lower $\delta^{2}H$–CH_4 values <−250‰, suggesting that it is not generated by thermal cracking of *n*-alkanes but rather that it has a deep Archaeal origin. The presence of petroleum-type hydrocarbons is consistent with a thermogenic origin, and at sites where CH_4 is predominant support the suggestion that gases have experienced extensive transport during which they mobilized oil from sediments ~2–4 km deep. These fluids then migrate into shallower, thermally immature muds, driving their mobilization and extrusion at the seafloor. At Porto MV, the limited presence of petroleum in mud breccia sediments further supports the hypothesis of a predominantly deep microbial origin of CH_4.

1. Introduction

Sub-marine mud volcanoes (MVs) provide an important pathway for the expulsion of fluids and light volatile hydrocarbon gases from dewatering sedimentary wedges in collisional settings or subduction zones (e.g., Milkov, 2005). Generation and expansion of hydrocarbon gases due to depressurization during transport is thought to constitute a major driving factor in sustaining the buoyant ascension of fluidized mud and clasts (i.e., mud breccia) and its breaching to the

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doi:10.1016/j.chemgeo.2009.06.023

seafloor (e.g., Hedberg, 1974; Brown, 1990). In spite of their key role in cold seep processes, investigations into the origins of light volatile hydrocarbon gases in such environments (Charlou et al., 2003; Blinova et al., 2003; Schmidt et al., 2005; Stadnitskaia et al, 2006; Mastalerz et al., 2007) rely almost entirely on the analysis of their molecular and stable isotopic compositions. Although models based on these parameters provide broad constraints for the formation of sedimentary hydrocarbon gases (Bernard et al., 1978; Schoell, 1980; Whiticar et al., 1986; Chung et al., 1988), major uncertainties remain for a wide range of environmental conditions (e.g., production by methanogenic *Archaea*, Valentine et al., 2004 and references therein; abiogenic generation, McCollom and Seewald, 2006; Horita and Berndt, 1999) and with regard to the effects of transport (Fuex, 1980; Prinzhofer and Pernaton, 1997). At cold seeps, these uncertainties are exacerbated by the fact that hydrocarbon gases vented at the seafloor or in the shallow subsurface may have experienced post-generational alteration during migration (e.g., James and Burns, 1984). Previous investigations of Gulf of Cadiz MVs have reported on the deep thermal origin of the light volatile hydrocarbon gases vented in this cold seep province (Mazurenko et al., 2002, 2003; Stadnitskaia et al., 2006; Hensen et al., 2007), and studies on lipid biomarkers and microbial activity at three MVs showed the occurrence of seep-related anaerobic oxidation of methane (AOM) in the past and present (Niemann et al., 2006; Stadnitskaia et al., 2008). In this study, we evaluate the conclusions of previous efforts by combining analyses of the molecular and isotopic composition of hydrocarbon gases with the organic geochemistry of the sediments to infer the depth of formation of hydrocarbon gases compared to that of fluids (Hensen et al., 2007) and of mobilized mud. Our approach shows that multiple gas sources and transport pathways occur in different areas of the tectonically active sedimentary wedge.

2. Sampling and methods

2.1. Sediment sampling

Sediment, fluid, and gas samples were recovered by gravity coring from eleven active MVs throughout the Gulf of Cadiz during the *RV-Sonne* SO 175-2 cruise in 2003 (Kopf et al., 2004), the *RV-Merian* MSM1 cruise in 2006 and the *RV-Professor Logachev* TTR-14, -15 and -16 cruises in 2004, 2005 and 2006, respectively. The sites sampled during the different expeditions are presented in Table 1 and shown in Fig. 1. The cores were segmented into 1 m lengths and cut lengthwise in a cooled laboratory at ~6 °C (except onboard the *RV-Professor Logachev*). Sediment samples were collected within 1–2 h after core retrieval. Gas hydrate samples were obtained from Porto, Captain Arutyunov and Bonjardim MVs (Table 1).

2.2. Light volatile hydrocarbon gases

Light hydrocarbon gases were stripped from mud samples onboard according to the headspace equilibration method of McAullife (1971) modified as described in Bowes and Hornibrook (2006). The gas samples were stored by displacement in glass vials filled initially with pH = 1, 10% KCl solution to avoid air contamination and microbial alteration. Concentrations of light volatile hydrocarbon gases were

Table 1
Site location, water depth and core identification for the mud volcanoes sampled in this study.

Site	Core ID	Core type	Longitude (°W)	Latitude (°N)	Water depth (m)	Core length (cmbsf)	Gas hydrate	Cruise
Bonjardim MV	GeoB9051	Gravity core	09°00.03′	35°27.61′	3087	250	Inferred	SO-175-2
	MSM1-130	Gravity core	09°00.14′	35°27.81′	3048	280		MSM1
	AT624	Gravity core	08°59.84′	35°27.56′	3065	205	Recovered	TTR-16
Carlos Ribeiro MV	MSM1-154	Gravity core	8°25.35′	35°47.26′	2198	210	–	MSM1
	AT613	Gravity core	8°25.24′	35°47.26′	2204	251	–	TTR-16
	AT614	Gravity core	8°25.30′	35°47.25′	2210	85	–	TTR-16
	AT616	Gravity core	8°25.30′	35°47.25′	2200	167	Inferred	TTR-16
Olenin MV	AT626	Gravity core	8°37.54′	35°35.00′	2628	470	No	TTR-16
Soloviev MV	AT619	Gravity core	9°06.45′	35°12.78	3295	117	Inferred	TTR-16
Semenovitch MV	AT592	Gravity core	9°05.24′	35°13.42′	3242	205	–	TTR-15
	AT620	Gravity core	9°05.20′	35°13.43′	3243	143	Inferred	TTR-16
Porto MV	AT596	Gravity core	9°30.53′	35°33.81	3878	165	Inferred	TTR-15
	MSM1-143	Gravity core	09°30.44′	35°33.70′	3862	115		MSM1
	MSM1-163	Gravity core	09°30.483′	35°33.734′	3861	–	Recovered	MSM1
	AT621	Gravity core	9°30.40′	35°33.78′	3921	140	–	TTR-16
	AT623	Gravity core	9°30.46′	35°33.76′	3875	150	Inferred	TTR-16
Captain Arutyunov MV (CAMV)	GeoB9041	Gravity core	7°19.97′	35°39.70′	1313	200	Small crystals observed	SO-175-2
	GeoB9072	Gravity core	7°19.95′	35°39.71′	1321	325	Small crystals observed	SO-175-2
	GeoB9036	TV-Grab	7°19.96′	35°29.68′	1320	–	Recovered	SO-175-2
	AT543	Gravity core	7°19.98′	35°39.69′	1345	160	Small crystals observed	TTR-14
	AT545	Gravity core	7°20.06′	35°39.69′	1337	300	Small crystals observed	TTR-14
	AT548	Kasten core	7°20.03′	35°39.70′	1345	150	Small crystals observed	TTR-14
	MSM1-205	Gravity core	7°20.08′	35°39.69′	1326	350		MSM1
	MSM1-174	Gravity core	7°19.95′	35°39.73′	1323	305		MSM1
	MSM1-218	Box core	07°20.01′	35°39.69′	1318		Recovered	MSM1
Ginsburg MV	GeoB9061	Gravity core	7°05.29′	35°22.42′	911	110	Small crystals observed	SO-175-2
	AT521	Gravity core	7°05.28′	35°22.28′	919	216	Small crystals observed	TTR-14
	AT522	Gravity core	7°05.30′	35°22.42′	912	202	–	TTR-14
Mercator MV	MSM1-239	Gravity core	6°38.70′	35°17.91′	353	200	–	MSM1
	MSM1-263	Gravity core	6°38.79′	35°17.86′	351	135	–	MSM1
Meknes MV	AT540	Gravity core	7°04.41′	34°59.07′	701	115	–	TTR-14
	AT542	Gravity core	7°04.36′	34°59.18′	703	90	–	TTR-14
	AT580	Gravity core	7°04.35′	34°59.20′	705	72	–	TTR-15
Shouen MV	AT612	Gravity core	7°15.47′	35°28.45′	1180	132	–	TTR-16

SO-175-2: *RV-Sonne* cruise SO175-2.
MSM1: *RV-Merian* cruise MSM1.
TTR-14, 15, 16: *RV-Professor Logatchev* cruises TTR-14, 15, and 16.