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Geochemical evidence for biogenic methane production and consumption in the shallow sediments of the SE Mediterranean shelf (Israel)



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ABSTRACT

This study presents geochemical evidence for biogenic methane formation (methanogenesis) in the shallow sediments of the oligotrophic SE Mediterranean continental shelf at water depths between 46 and 88 m. Depth-profiles of methane concentrations and related chemical parameters such as dissolved sulfate, dissolved inorganic carbon (DIC), and the stable carbon isotope composition of DIC and methane ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{CH}_4}$, respectively) were measured in six sediment cores (each 4.2–5.4 m long) in order to characterize the processes that involve methane production and decomposition. All the sediment cores reached the consumption depth of the entire sulfate pool and the *in-situ* microbial methane production (methanogenesis) zone. Methane concentrations reached saturation levels in one of the cores, but not in the others, probably because the zone of maximum methanogenesis was at a greater depth. Although the sediments exhibit a low TOC content of $\sim 1\%$, the biogenic methane formation indicates a relatively high organic carbon lability capable of sustaining all redox microbial activity potential. Anaerobic oxidation of methane (AOM) was also evident in the sulfate–methane transition zone, showing a distinct isotope signature in diffusion limited conditions.

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1. Introduction

Methane (CH_4) is an important natural gas used as an energy source, but also an effective greenhouse gas whose atmospheric concentration has more than doubled since preindustrial time, to values about 1800 ppbv (Hartmann et al., 2013). It is emitted from both anthropogenic and natural sources, and the emissions are estimated to be about 304–368 and 238–484 $T_g \text{ CH}_4 \text{ yr}^{-1}$ ($T_g = 1 \times 10^{12} \text{ g}$), respectively as mentioned in the IPCC 2013 report (Stocker et al., 2013). The major natural fluxes originate from the terrestrial environment; however, marine sediments are highly important as well, as they contain the largest natural reservoir of methane despite their low emission fluxes ($\sim 3\%$) (Archer, 2007).

Natural sources of methane originate from microbial processes that take place in organic rich sediments (methanogenesis, e.g. (Whiticar, 1999)), or from kerogens following thermochemical reactions at high temperatures and pressures (thermogenic

methane, e.g. (Schoell, 1988)). Methanogenesis is the final process of microbial organic matter mineralization in anaerobic environments, after all other electron acceptors (O_2 , NO_3 , Mn(IV) , Fe(II) and SO_4) have been exhausted (Froelich et al., 1979). In freshwater sediments the dominant pathway for methanogenesis is acetate fermentation (acetoclastic methanogenesis, Eq. (1)), whereas in marine sediments it is CO_2 reduction by hydrogen (hydrogenotrophic methanogenesis, Eq. (2)) (Whiticar et al., 1986)

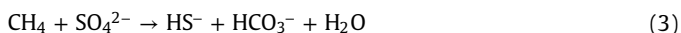


When the produced methane diffuses into contact with an available electron acceptor it can be consumed by microbial oxidation (methanotrophy). Methanotrophy is the main process that prevents the escape of methane into the atmosphere. In oxic water methanotrophic bacteria are responsible for oxidizing methane into CO_2 , using O_2 as an electron acceptor (Chistoserdova et al., 2005). In marine sediments anaerobic oxidation of methane (AOM), coupled to sulfate reduction as shown in Eq. 3 (Hoehler

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et al., 1994), was found to consume up to 90% of the upward-diffused methane at the sulfate-methane transition zone (SMTZ), thus preventing its release from this huge reservoir into the atmosphere (Valentine, 2002). Frequently, most of the sulfate is reduced by this process (e.g. Niewöhner et al., 1998; Boetius et al., 2000; Aharon and Fu, 2000; Sivan et al., 2007).



The AOM process typically involves a microbial consortium of archaea and bacteria that are affiliated with Methanosarcina-type methanogens and sulfate-reducing bacteria, respectively (Boetius et al., 2000; Orphan et al., 2002; Thauer, 2011). It seems that anaerobic methanotrophic archaea (ANME) oxidize the methane, while the bacterial partner uses the resulting reducing equivalents to reduce sulfate (Thauer and Shima, 2006; Basen et al., 2011). Recently, however, AOM mediated solely by archaea was reported (Milucka et al., 2012), in which the archaea was shown to oxidize the methane and reduce the sulfate to elemental sulfur.

Methanogenesis and methanotrophy processes have also been studied using a geochemical isotopic approach. Carbon isotopes provide a good constraint on the depth distribution and location of methanogenesis and methanotrophy and can be used to quantify these processes due to the large carbon isotopic fractionation associated with both methane production and consumption (e.g. Whiticar, 1999; Borowski et al., 2000; Sivan et al., 2007; Adler et al., 2011). During methanogenesis, ^{12}C is strongly partitioned into methane; the $\delta^{13}\text{C}$ of the methane produced can vary between -50% and -100% . In contrast, the residual dissolved inorganic carbon pool becomes highly enriched in ^{13}C , occasionally by as much as $50\text{--}70\%$. Oxidizing this methane during AOM, on the other hand, results in ^{13}C -depleted dissolved inorganic carbon (DIC) and in slightly heavier $\delta^{13}\text{C}$ values of the residual methane, due to both a fractionation of $0\text{--}10\%$ during the oxidation of methane and to the initial $\delta^{13}\text{C}$ value of the methane itself (Alperin et al., 1988; Martens et al., 1999). Typically, thermogenic methane is enriched in ^{13}C compared to microbial methane, having $\delta^{13}\text{C}_{\text{CH}_4}$ values that range between approximately -50% and -20% (Whiticar, 1999).

Methane-related processes in the sediments of the Eastern Mediterranean Sea are of great importance, from both the economic and the environmental aspects. Recently, large gas fields from the deep geological layers of the Oligocene–Miocene era were discovered in sediments in the deep water (> 1500 m) of the SE Mediterranean Sea (Levantine basin) (Gardosh and Tannenbaum 2014). Methane seeps were also found in the deep sea sediments (Omeregic et al., 2009, 2008; Rubin-Blum et al. (2014). However, methane production in the shallow sediments of the SE Mediterranean continental shelf has not been assumed due to its current oligotrophic conditions (Low nutrient, low chlorophyll; Herut et al., 2000; Kress et al., 2014), which offer a relatively low content of organic carbon in the sediment ($< 1\%$). Schattner et al. (2012) interpreted a band of high amplitude scattered reflectivity

observed in high (~ 0.3 m) resolution seismic profiles across the continental shelf of northern Israel to reflect the presence of a 'gas front' within the seafloor sediments at water depths between 37 and 112 m. They also repeatedly (for over 3 years) observed acoustic reflectivity in the water above the seafloor, which they suggested represents a long term active gas seepage.

This study aimed to test whether there is methane formation in the shallow sediments of the oligotrophic SE Mediterranean continental shelf, and to characterize the major sinks and sources of methane in the shelf, including their depth distribution. This was achieved by using a geochemical approach similar to the one used in our work on sediments from estuaries (Antler et al., 2014) and lakes (Adler et al., 2011; Sivan et al., 2011). For the first time in this area, we were able to collect, several sediment cores 5–6 m long from the continental shelf of Israel and to perform depth profiles of methane and its related parameters in the pore water (dissolved sulfate, dissolved inorganic carbon (DIC) and the stable carbon isotope composition of DIC and methane ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{CH}_4}$, respectively)).

2. Materials and methods

2.1. Sampling

Six sediment cores were collected from the undisturbed seafloor sediments of the Mediterranean continental shelf of Israel at water depths between 49 and 88 m (Table 1 and Fig. 1), during two cruises on the R.V. *Shikmona* that took place on August 2013 and February 2014. The sediment cores (each 4.6–5.4 m long) were collected using a Benthos 2175 piston corer. The study site locations were chosen based on the mapping of a sub-bottom depth high amplitude scattered reflectivity layer, interpreted to be related with the presence of free gas bubbles (e.g. (Schattner et al., 2012) 'Gas Front'), as observed in high (~ 0.3 m) resolution seismic profiles collected between 2008 and 2013 by Moses Strauss, as well as additional unpublished data). The actual coring locations generally correspond to relatively shallow interpreted gas related reflectivity.

The sediment cores were sliced onboard at intervals of 40–50 cm within minutes of extracting the core from the seafloor. About 1.5 ml from the edge of each sediment slice was immediately transferred into N_2 -flushed crimp bottles containing 5 ml of 1.5 N NaOH for the headspace measurements of CH_4 and $\delta^{13}\text{C}_{\text{CH}_4}$ (after Adler et al., 2011). Subsamples of 100 ml from the edge of each sediment slice were stored in vials under anaerobic conditions and pore water was extracted from them on the same day by centrifugation at 4°C under a N_2 atmosphere. The supernatant was filtered through $0.45\ \mu\text{m}$ filters. The sediment was measured for its total organic carbon (TOC) content during the February cruise.

Table 1
The cores sampling dates, positions, water depths and length retrieved.

Sampling date	Core name	Water depth (m)	Retrieval (m)	Location	Latitude (N)	Longitude (E)
August 14, 2013	PC-3	81	5.1	Offshore Haifa	32°55.29'	34°54.14'
	PC-5	87	4.6	Offshore Haifa	32°55.47'	34°54.01'
	PC-6	49	4.5	Offshore Netanya	32°17.11'	34°44.62'
February 6, 2014	PC-3-14*	82	4.8	Offshore Haifa	32°55.30'	34°54.14'
	NRD	81	5.35	Offshore Acre	32°59.63'	34°56.27'
	SG1	88	4.2	Offshore Acre	32°57.83'	34°55.29'

* Core PC-3-14 was sampled on February, 2014, in proximity to the sampling position of core PC-3 on August, 2013.

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