Proposed sources of methane along the Dead Sea Transform

N. Avrahamov [a,b], F. Gelman [b], Y. Yechieli [b,c], Z. Aizenshtat [d], A. Nissenbaum [e], O. Sivan [a,*]

[a] Department of Geological and Environmental Sciences, Ben Gurion University of the Negev, Beer-Sheva, Israel
[b] Geological Survey of Israel, Jerusalem, Israel
[c] Department of Environmental Hydrology and Microbiology, Zuckerberg Institute for Water Research, Blaustein Institutes for Desert Studies, Ben Gurion University of the Negev, Israel
[d] Institute of Chemistry, Hebrew University, Jerusalem, Israel
[e] Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel

ABSTRACT

The concentrations and isotopic compositions of methane, higher alkanes, dissolved inorganic carbon (DIC) and CO_2 were studied in fresh groundwater, brines and springs along the Dead Sea Transform (DST), from the Hula Valley in the north to the Dead Sea (DS) basin in the south. Although the occurrence of methane along the DST was documented before, this is the first time that comprehensive research was conducted on the methane provenance and the post-genetic reactions involved. The methane stable carbon isotopic composition ($\delta^{13}C_{CH4}$) shows a distinct geographic pattern. In the northern part of the DST studied, in the Hula valley and Lake Kinneret, where recent marshy and lacustrine environments exist, the methane source seems to be related to intense shallow depth methanogenesis. This microbial methane shows low ^{13}C values in the range of $\delta^{13}C_{CH4}$ between −58‰ and −72‰ and high alkane ratios ($C_1/C_2 + C_3$) between 100 and 1000. The isotope fractionation $\alpha_{CO2–CH4}$ of 1.065‰ suggests the domination of hydrogenotrophic methanogenesis rather than acetoclastic methanogenesis. In the waters of Hammat Gader and Tiberias hot spring, whose source is the Cretaceous aquifer, $\delta^{13}C_{CH4}$ has high values of −28‰ and −56‰, respectively, with low alkane ratios of ~40 in both sites. The high δ^2H_{CH4} values of Hammat Gader, in addition to the isotopic composition of the DIC and the difference between CO_2 and CH_4, reject the possibility of local microbially produced methane and suggest a sub-surface thermogenic source of an initial stage of thermal degradation of bituminous chalk of Senonian age. Similarly, methane in groundwater from the DS basin is also interpreted to be of thermogenic origin. In accordance with the local geology context in the DS basin of buried asphalt, and due to the low geothermal gradient in the region, it is speculated that methane is produced from slight heating of the asphalts. In general, it seems that there is a thermogenic methane contribution along the entire DST, which is locally masked by high microbial activity in shallow organic-rich environments, such as Lake Kinneret and the Hula basin.

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1. Introduction

Methane (CH_4, C_1) is known to be formed via three possible mechanisms: thermogenic (Schoell, 1988), microbial (methanogenesis, Whiticar, 1999), and abiotic (Etiope and Lollar, 2013). *Thermogenic methane* is produced by thermochemical reactions and can be classified according to the source rock type (kerogen type) and the maturity level from which it originated. In general, thermogenic methane is enriched in ^{13}C compared to microbial methane, which has $\delta^{13}C_{CH4}$ values from ~ −50‰ to −20‰ (Whiticar, 1999). The δ^2H of thermogenic methane ranges from ~ −275‰ to −100‰. However, there is considerable overlap in δ^2H_{CH4} between certain microbial and thermogenic methane types (Whiticar, 1999).

Microbial methane is produced mainly by two pathways: acetate fermentation (acetoclastic methanogenesis) and CO_2 reduction

(hydrogenotrophic methanogenesis). These two methanogenesis pathways can be tracked with the aid of carbon and hydrogen isotopes. In both cases, as a result of preferential utilization of ^{12}C from the dissolved inorganic carbon (DIC) pool for methane formation, the DIC becomes enriched in ^{13}C, often by as much as 70‰ (Whiticar, 1999; Borowski et al., 2000), and according to the fractionation factor between the carbon species, the CO_2 is expected to be 8‰ lower than the DIC value. However, the reduction of CO_2 to methane is usually associated with higher isotopic fractionation, causing highly depleted methane with $\delta^{13}C_{CH4}$ values as negative as −110‰ (Whiticar, 1999). The isotopic fractionation of methane associated with the fermentation of acetate is lower, with $\delta^{13}C_{CH4}$ values of −50‰ to −60‰ (Whiticar, 1999). Similar to the carbon isotope, the hydrogen isotopes also have a wide range of δ^2H values, from −400‰ to −150‰. The borderline δ^2H value between the two methanogenesis pathways is ~ −250‰, with higher deuterium values for the hydrogenotrophic methanogenesis. As during both methanogenesis pathways basically only methane is produced (and not higher hydrocarbons), methanogenesis

areas are characterized by very high $C_1/(C_2 + C_3)$ ratios ranging between 10^3 and 10^5. Microbial oxidation of hydrocarbons can change this ratio, challenging the interpretation of the methane source. In some anoxic environments "non-competitive" substrates such as methylated amines, methanethiol, and dimethyl sulfide are utilized by methanogens (Oremland et al., 1982a; King et al., 1983; Kiene et al., 1986; Summons et al., 1998; Whiticar, 1999). Non-competitive substrates can be derived from the decomposition of organic matter, such as methanol from plant lignins and pectins (Schink and Zeikus, 1980; Oremland et al., 1982a) and methylamines from salt marsh vegetation. In saline environments such as the Big Soda Lake, Nevada, methanol serves as a substrate to the methane production (methylotrophic methanogenesis; Oremland et al., 1982b). Even though the contribution of methanol to total methane production may be limited in the environment, methanol may significantly affect the carbon isotopic signature of the methane produced, since carbon isotopes seem to be strongly fractionated in this pathway, ranging between 72‰ and 83‰ (Penger et al., 2012).

The third mechanism for methane production is *abiotic reaction*, divided into two main major classes: (1) mantle-magmatic processes, which include methane resulting from high-temperature reactions in the mantle; and (2) gas–water–rock reactions, which are inorganic syntheses independent of the presence of magma or magma derived fluids (Etiope and Lollar, 2013 and references therein). In general, abiotic methane is distinguished from the microbial and thermogenic methane by an overall shift toward more ^{13}C and ^{2}H enriched values. The $\delta^{13}C$ and $\delta^{2}H$ of abiotic methane range from ~ 0‰ to −40‰ and −99‰ to −244‰, respectively, partially overlapping with both the microbial and thermogenic fields (Etiope and Lollar, 2013). Within the abiotic methane group, there is an apparent trend toward more ^{13}C and ^{2}H enriched values in the high-temperature volcanic-hydrothermal systems and in the serpentinized ultramafic rocks ($\delta^{13}C_{CH4}$ of −20‰ to −5‰ and $\delta^{2}H_{CH4}$ higher than ~ −250‰). In contrast, more ^{13}C-^{2}H depleted values appear to be closely associated with gases found in the Precambrian crystalline igneous rocks ($\delta^{13}C_{CH4}$ of −40‰ to 30‰, and $\delta^{2}H$ more depleted than ~ −250‰) (Etiope and Lollar, 2013).

Due to the geological setting along the active Dead Sea Transform (DST) (Smit et al., 2010), in which a large geological sequence is buried, the three known mechanisms for methane genesis can be considered feasible and are discussed in the present study. Although the DST has been a target for asphalt, oil and gas exploration, only limited and sporadic data on the presence and isotopic composition of the gas along the transform were reported (Amit and Bein, 1979a; Nissenbaum and Goldberg, 1980; Nissenbaum et al., 1988; Nissenbaum, 1993). Therefore, the objective of the present study is to constrain the methane origins and the post-genetic reactions that could affect its isotopic composition in three basins along the DST, from the north to the south: the Hula basin; the Kinnarot basin, including Lake Kinneret (Sea of Galilee); and the Dead Sea (DS) basin, including the Sedom salt plain (Fig. 1).

1.1. Geological and hydrogeological setting

The Dead Sea Transform (DST) forms part of the plate boundary between the African and Arabian plates in what might be considered a single geological system. In Israel, which is the southern segment of the DST, the transform is marked by an almost continuous valley, with a series of deep pull-apart basins that are separated by less pronounced saddles (e.g., Garfunkel, 1981; Garfunkel and Ben-Avraham, 1996) including the Hula basin, the freshwater Lake Kinneret (Sea of Galilee), the hypersaline Dead Sea (Garfunkel, 1981) and the Arava valley. The deep base level of the transform serves as a discharge area for the draining
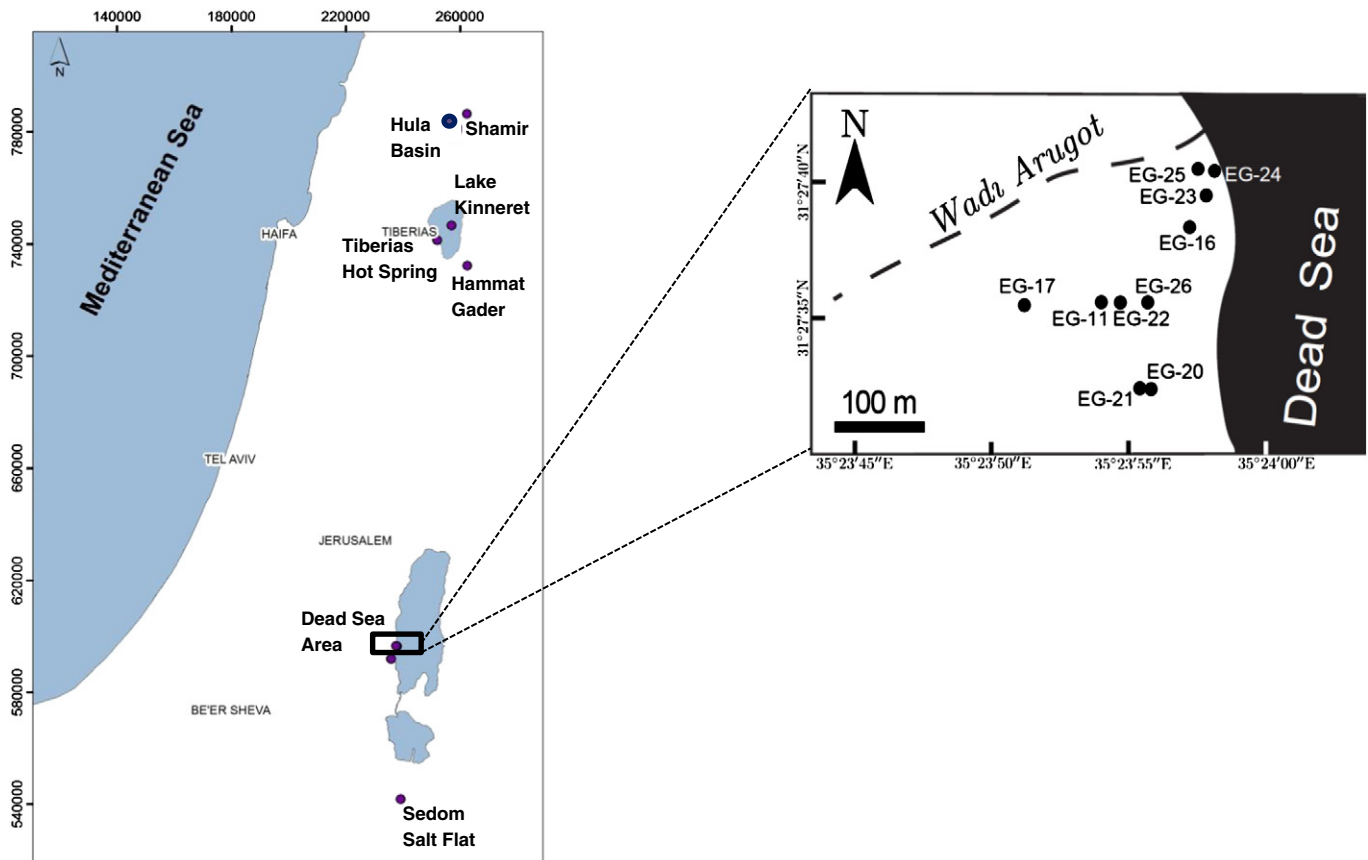

Fig. 1. A location map of the study areas including the research well distribution and Tiberias hot spring.