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Comment

Methane origin in the Samail ophiolite: Comment on “Modern water/rock reactions in Oman hyperalkaline peridotite aquifers and implications for microbial habitability” [Geochim. Cosmochim. Acta 179 (2016) 217–241]

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Miller et al. (2016) report a new study of fluids in the peridotites of the Samail ophiolite in Oman related to modern serpentinization (olivine hydration), a process that can provide energy and raw materials for chemosynthetic microbial life. The authors, in particular, report an isotopic composition for methane (CH_4) in groundwater near Ibra (up to 1.4 mM) that is unusually ^{13}C-enriched ($\delta^{13}C_{CH4} \sim +2.4$ and +3‰ VPDB), and consider the gas origin to be uncertain, i.e., abiotic or microbial, and to be modulated by significant fractionation due to oxidation or diffusion. The purpose of this comment is to clarify and correct a few points concerning the possible origin of the $\delta^{13}C_{CH4}$ values, with the intention to promote a fruitful and constructive debate, considering the interest that there is for serpentinization and the associated formation of various gases.

The CH_4 data from Miller et al. are re-examined in a global context of gas in serpentinized peridotites and, in particular, by considering published data (isotope composition of CH_4 and concentrations of C_{2+} alkanes) also obtained from the Samail ophiolite, data neglected by the authors. These data significantly impact the interpretation of Miller et al. concerning the possibility that methane can be microbial. Potential isotopic fractionations by oxidation or diffusion, evaluated considering $\delta^{13}C_{CH4}$–δ^2H_{CH4} correlated variations, the occurrence of significant amounts of ethane and propane in the Oman ophiolite aquifers and Rayleigh fractionation analysis suggest that methane can hardly be considered microbial. Isotopic fractionations, however, are not necessary to explain the unusual $\delta^{13}C_{CH4}$ values: an alternative hypothesis is that methane carbon may derive from ^{13}C-enriched carbonates occurring below the Samail ophiolite nappe, a hypothesis not considered by Miller et al.

1. THE IBRA BOREHOLE $\delta^{13}C_{CH4}$ VALUES ARE NOT THE HIGHEST OBSERVED TO DATE

A first note addresses the singularity of the $\delta^{13}C_{CH4}$ values. Miller et al. claimed (in the Abstract and on page 233) that the CH_4 they analyzed has the heaviest carbon (the most ^{13}C-enriched) reported in the literature to date ($\delta^{13}C_{CH4} \sim +2.4$ and +3‰ VPDB). Their statement is not correct. Much more ^{13}C-enriched CH_4 values, with $\delta^{13}C_{CH4}$ up to +21‰, were reported by Potter et al. (2004) for gas measured in the German Zechstein (Permian) evaporite; this ^{13}C enrichment was likely due to evaporation of brines.

2. GLOBAL CONTEXT AND NEGLECTED GAS GEOCHEMICAL DATA

The Samail ophiolite in Oman is one of tens of sites in the world where methane related to active serpentinization has been reported since the 1980s (e.g., Etiope and Schoell, 2014). To date, CH_4-rich hyperalkaline waters and/or gas seeps issuing from faulted peridotites have been documented in at least 16 countries (in Oman as well as in the

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Philippines, New Zealand, Turkey, Italy, Greece, Portugal, Spain, United States - California, Costa Rica, Japan, the United Arab Emirates, Canada, New Caledonia, Norway, and Serbia). Whenever stable C and H isotope ratios of CH_4 are analyzed together, a dominant abiotic origin of the gas, related to the reduction of a C compound (generally CO_2) via Fischer–Tropsch or Sabatier reactions, has been suggested (with the exception of The Cedar springs in California that release dominantly microbial CH_4; Wang et al., 2015). At least 60 hyperalkaline springs, some displaying free gas bubbling, have been documented within the Samail ophiolite in Oman (Neal and Stanger, 1983). Fritz et al. (1992) were the first to report the stable C and H isotopic composition of CH_4 within the Samail peridotite and to propose an abiotic origin. Successive works (Sano et al., 1993; Boulart et al., 2013) also suggested inorganic reactions as the source of gas and excluded microbial origins. Recently, Etiope et al. (2015) reported a typical abiotic isotopic composition of CH_4 within the Samail peridotite aquifer in the United Arab Emirates. Unfortunately, Miller et al. did not take into account all these publications, which provide a useful reference for better evaluating methane origin in the two boreholes investigated.

3. REASSESSING CH_4 ORIGIN

Fig. 1 provides the new isotope data of Miller et al. (boreholes NSHQ) together with the data of Fritz et al. (1992), Sano et al. (1993), and Etiope et al. (2015) for the Samail ophiolite. Additional values are provided for all other continental serpentinization sites discovered to date. The new Samail data of Miller et al. are actually the most ^{13}C-enriched among the serpentinization sites and fall near the traditionally defined abiotic range. CH_4 in Oman hyperalkaline waters has a variable isotopic signature: $\delta^{13}C$ is −34‰ at Ain Al-Waddah (Sano et al., 1993) and approximately −12 to −15‰ at Nizwa and Al Khoud (Fritz et al., 1992). Miller et al. suggested that methane at Ibra, with a $\delta^{13}C_{CH4} \sim +2.4$ and +3‰, could be abiotic or microbial, since they detected some methanogens in the water. In any case Miller et al. outline that methane would be affected by extensive fractionation due to biological oxidation or diffusion, with both processes enriching the residual methane in ^{13}C. In both cases, as the authors admit, methane should also be enriched in ^2H, a finding that was not observed. Nevertheless, in the Conclusions section, the authors kept a microbial origin hypothesis without explaining how microbial gas, even after oxidation, could have acquired a combination of "abnormal" (positive) $\delta^{13}C_{CH4}$ values and "normal" δ^2H_{CH4} values. The wide range of $\delta^{13}C_{CH4}$ values of the Samail ophiolite fluids, now shown in Fig. 1, can be due to different carbon feedstocks, temperatures of C reduction and degree of reaction completeness (Etiope and Ionescu, 2015).

3.1. Microbial methane origin?

The microbial oxidation of methane produces $\delta^{13}C_{CH4}$–δ^2H_{CH4} correlated variations with $\Delta H/\Delta C \sim 8$–9 (Alperin et al., 1988; Feisthauer et al., 2011). ΔH and ΔC are the respective variations in δ^2H_{CH4} and $\delta^{13}C_{CH4}$ values: when the $\delta^{13}C_{CH4}$ value increases by 1‰, the corresponding δ^2H_{CH4} value increases by ~8–9‰. Following this trend (red arrow in Fig. 1), it is clear that NSHQ methane cannot

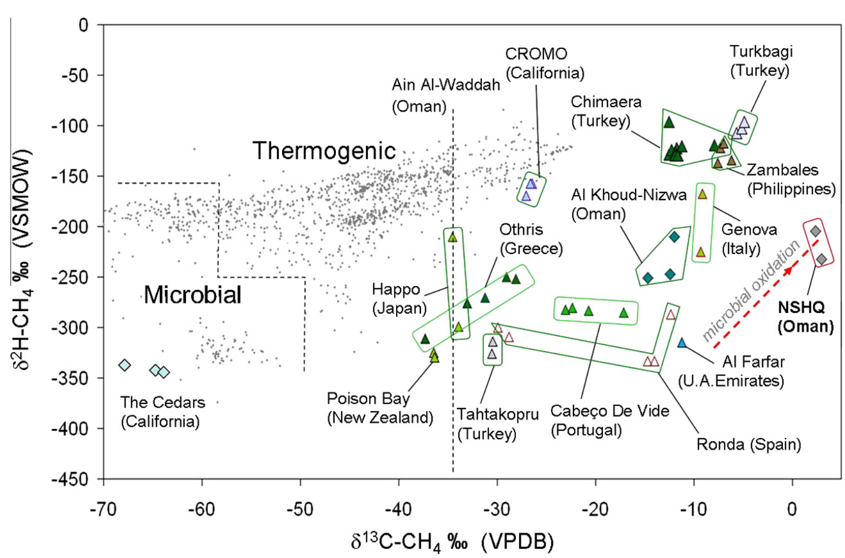

Fig. 1. The deuterium and carbon isotope ratios of methane reported by Miller et al. (2016) (NSHQ) as compared to other sites located within the Samail ophiolite (Oman and United Arab Emirates), land-based serpentinization sites worldwide, and global data-sets of biotic (microbial and thermogenic) gas (data from Etiope and Schoell, 2014; Wang et al., 2015; Etiope et al., 2016). Only $\delta^{13}C$ was analysed for the Ain Al-Waddah spring (vertical dashed line; Sano et al., 1993). The red arrow shows the microbial oxidation trend ($\delta^{13}C_{CH4}$–δ^2H_{CH4} correlated variations with $\Delta H/\Delta C \sim 8$–9), as explained in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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