

# Lawrence Berkeley National Laboratory

## LBL Publications

### Title

Reply to "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]

### Permalink

<https://escholarship.org/uc/item/25k0f17q>

### Authors

Miller, Hannah M  
Matter, Jürg M  
Kelemen, Peter  
et al.

### Publication Date

2017

### DOI

10.1016/j.gca.2016.11.011

Peer reviewed

# Reply to “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]

Author links open overlay panel [Hannah M. Miller<sup>a</sup>](#) [Jürg M. Matter<sup>b,c</sup>](#) [Peter Kelemen<sup>c</sup>](#) [Eric T. Ellison<sup>a</sup>](#) [Mark Conrad<sup>a</sup>](#) [Noah Fierer<sup>e</sup>](#) [Tyler Ruchala<sup>a</sup>](#) [Masako Tominaga<sup>a</sup>](#) [Alexis S. Templeton<sup>a1</sup>](#)  
Show more

<https://doi.org/10.1016/j.gca.2016.11.011> Get rights and content

## Refers to

Giuseppe Etiope

[Download PDF](#)

- [Previous article in issue](#)
- [Next article in issue](#)

We thank Dr. Giuseppe Etiope for his comment and the opportunity to further discuss why we consider the origin of the [methane](#) detected in subsurface fluids obtained from a [peridotite aquifer](#) in Oman to be enigmatic.

The central focus of [Miller et al. \(2016\)](#) was the characterization of the fluids and [dissolved gases](#) recovered from 300 meter wells drilled into [peridotite](#) at two locations near Ibra. [Microscale](#) geochemical analyses of rock chips recovered during drilling gave further insight into the aqueous geochemistry measurements. These samples allowed us to analyze the extent of modern peridotite hydration and secondary mineralization in light of potential hydrogen-generating reactions. Additionally, biomass was recovered from the fluids, and 16S rRNA showed the presence of [methanogens](#) and methanotrophs. These methane-cycling microbes may be modulating the isotopic signature of CH<sub>4</sub> found in the wells; thus, we do not feel comfortable rejecting the hypothesis that [microbial activity](#) contributes to the unusual isotopic signature of CH<sub>4</sub> in the wells without further investigation.

The comment by [Etiope \(2016\)](#) is entirely directed towards the interpretation of the two [methane](#) δ<sup>13</sup>C and δD values reported. [Miller et al. \(2016\)](#) simply hypothesized about possible origins of the CH<sub>4</sub> and offered several potential processes, both abiotic and biotic, which could contribute to the positive δ<sup>13</sup>C observed in the CH<sub>4</sub>. We recognize this is a complex topic because numerous physical, chemical and biological processes likely modulate the residence time and reaction histories of the fluids that were sampled, as well as the concentrations and [isotopic composition](#) of the gases. We are now conducting more comprehensive studies to understand the coupled abiotic and biological processes that may give rise to hydrogen and methane cycling,

whereas [Miller et al. \(2016\)](#) simply presented novel data and discussed potential processes leading to the positive  $\delta^{13}\text{C}$   $\text{CH}_4$ . With the framework that identifying the origin of the methane was only a small portion of [Miller et al. \(2016\)](#), we will reply to Etiope's comment and engage in further debate.

[Etiope \(2016\)](#) makes the point that the  $\delta^{13}\text{C}$   $\text{CH}_4$  values found in subsurface Oman [boreholes](#) are the most positive  $\delta^{13}\text{C}$  values from a [serpentinization](#) site reported so far, but not the heaviest values reported in the literature as we asserted. We regret our error in the original paper and were interested to read the Potter et al. 2004 paper. However, [Miller et al. \(2016\)](#) did provide a global context for the  $\delta^{13}\text{C}$   $\text{CH}_4$  values measured near Ibra and gave examples of [methane](#) isotopic measurements from crystalline [bedrock](#) and/or serpentinization sites in the Zambales [ophiolite](#), Lost City, Canadian Shield, and Cedars ophiolite. Additionally, Fig. 2 showed how the  $\delta^{13}\text{C}$  values of dissolved methane samples at wells NSHQ04 and NSHQ14 compare to  $\text{CH}_4$  isotopic measurements from various sites around the world as presented in Etiope's extensive body of work on the subject ([Etiope et al., 2013](#)). [Etiope \(2016\)](#) has now contributed an excellent visual representation for several additional sites (see Fig. 1).

The [methane isotopic compositions](#) reported in [Miller et al. \(2016\)](#) do differ strongly from known isotopic compositions of biogenic methane. Currently, only abiogenic pathways are known to produce isotopically heavy methane values with  $\delta^{13}\text{C}$  values  $> -25\text{‰}$  ([Etiope and Schoell, 2014](#)).

[Etiope \(2016\)](#) proposes that the heavy  $\delta^{13}\text{C}$  of the NSHQ04 and NSHQ14 [methane](#) could be due to the reduction of isotopically heavy [dissolved inorganic carbon](#) derived from [Permian](#) carbonates underlying the [ophiolite](#). However, the geology of the Ibra area does not support this hypothesis. The [aquifer](#) intersected by wells NSHQ04 and NSHQ14 is in a relatively well-defined hydrological [catchment area](#) that does not contain any Coquina and Reefal [Limestone](#) (Permian) [outcrops](#). The Hawasina sediments (including carbonates) do underlie the ophiolite, and they do have [carbon isotope ratios](#) that are heavier,  $>0.5\text{‰}$ , ([Weyhenmeyer et al., 2002](#)) than the carbonate veins,  $-0.12$  to  $-9.64\text{‰}$  and DIC in alkaline [spring waters](#) in the [peridotite](#),  $-11.66$  to  $-23.67\text{‰}$  ([Kelemen et al., 2011](#)). If the Hawasina-derived carbonate is transferred into the peridotite aquifer, there should be an enrichment in the DIC  $\delta^{13}\text{C}$ , which is not observed. The peridotites and the Hawasina sediments are hydrologically separated by the metamorphic sole at the base of the ophiolite, which acts as a barrier to fluid exchange. This is supported by the occurrence of many springs along this contact, where large changes in [hydraulic conductivity](#) occur.

Fluid exchange between the [Permian](#) carbonates and the groundwater in NSHQ04 and NSHQ14 is considered unlikely. [Weyhenmeyer et al. \(2002\)](#) measured  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes of groundwater samples in the Samail [ophiolite](#) that varied from 0.7080 to 0.7088, which showed that the fluid chemistry was only affected by water/rock reactions with tertiary gravels and carbonate veins in the [peridotite](#). Similarly low  $^{87}\text{Sr}/^{86}\text{Sr}$  values have been measured by co-author Juerg Matter for fluids in NSHQ04 (0.705642) and in NSQH14 (0.707587). Underlying allochthonous [metasediments](#) of the Hawasina Group have a more radiogenic [strontium isotope](#) ratio  $>0.7100$ , including values as high as 0.7189 ([Weyhenmeyer et al., 2002](#), [Falk and Kelemen, 2015](#)). Although, low-grade portions of the metamorphic sole do have  $^{87}\text{Sr}/^{86}\text{Sr}$  values as low as 0.7061 ([Falk and Kelemen, 2015](#)), which allows the possibility that NSHQ14 fluids may have interacted with fluids in contact with the metamorphic sole. However, the proposal that carbon is transferred from [water/rock interaction](#) in the Hawasina [carbonate sediments](#) into the peridotite [aquifer](#) is unlikely.

[Etiopie \(2016\)](#) also hypothesizes that the  $\text{CH}_4$  migration pathways could be affected by salt diapirs in the area. However, the wells are north of the Ibra [salt dome](#), and the observations of Cooper et al. 2013 are not directly relevant; this study refers to a region in northern Oman, not in the Tayin Massif where the wells are situated.

We agree with [Etiopie and Schoell \(2014\)](#) that  $\text{CH}_4$  production is prevalent in hyperalkaline fluids hosted in serpentinites, such as the Type II fluids sampled in this study at NSHQ14 and NSHQ04. We also agree that [methane](#) likely forms through low temperature  $\text{CO}_2$ -reduction pathways that are abiotically catalyzed. Several works have invoked FTT or Sabatier reactions as an abiotic source of  $\text{CH}_4$  in sites of active [serpentinization](#). However, the reaction mechanism has not yet been directly constrained in low-temperature serpentinizing systems. Thus we caution against labelling these gasses as strictly abiotic. Such statements are too exclusive of physical and biological processes that may modulate  $\text{CH}_4$  gas concentrations and isotopic signatures, and they prevent continued evaluation of the reaction pathways operating in such [aquifers](#).

We reiterate that the coupled  $\delta\text{D}$  and  $\delta^{13}\text{C}$  [isotopic compositions](#) of the [methane](#) is most consistently interpreted as abiogenic according to empirically defined isotope fields ([Etiopie et al., 2013](#)), as well as in Figure 1 ([Etiopie, 2016](#)). [Miller et al. \(2016\)](#) and [Etiopie \(2016\)](#) both agree that when the methane originally formed, the  $\delta^{13}\text{C}$  was probably not as positive as is measured in our samples. Any action that significantly shifts the isotopic composition of the  $\delta\text{D}$  and  $\delta^{13}\text{C}$  of the methane will require significant loss and [distillation](#), such as diffusion or oxidation. This would imply extensive methane

consumption given the millimolar concentrations of dissolved methane measured in the deep well fluids. If methane does undergo significant aerobic biological oxidation in the shallow subsurface, we agree that the  $\Delta H/\Delta C$  for [methanotrophy](#) will impart a steep slope due to the strong kinetic [fractionation](#) imparted by methane monooxygenase during the irreversible breaking of the C–H bond ([Wang et al., 2016](#)). If we use the current  $\delta^{13}\text{C}$  and  $\delta\text{D}$  of the  $\text{CH}_4$  detected in wells NSHQ04 and NSHQ14 and trace backwards to a potential initial isotopic composition, those projected values will fall within a field empirically defined as abiotic, as shown by [Etiopie \(2016\)](#). Therefore, we concur that abiotic C reduction may well be the most likely mechanism of  $\text{CH}_4$  formation, as originally discussed by [Miller et al. \(2016\)](#).

However, we do not know the original  $\delta^{13}\text{C}$  and  $\delta\text{D}$   $\text{CH}_4$  and we do not have sufficient data points to define the field of possible  $\text{CH}_4$  [isotopic compositions](#) in the [aquifer](#); therefore, we also consider alternative processes that may have generated [methane](#) with unexpected initial isotopic compositions. [Miller et al. \(2016\)](#) aimed to characterize the water/rock reactions in the hyperalkaline aquifer that could sustain microbial life in the subsurface. The paper discussed how  $\text{CH}_4$  is relevant, because it can be both a product of [methanogenesis](#) and/or a potential electron donor for microbes in the subsurface. The aqueous geochemistry of the wells is favorable for anaerobic oxidation of methane (AOM) with sulfate, Fe(III)-oxides or nitrate as suitable electron acceptors. During AOM under energy-limited conditions, it is considered that  $\text{CH}_4$  is cycled under conditions of greater reversibility which could permit hydrogen exchange between  $\text{CH}_4$  and  $\text{H}_2\text{O}$ . Such reversible exchange would reset the methane  $\delta\text{D}$  towards an equilibrium value with cellular water during C–H bond breakage and reassembly (see [Wang et al., 2016](#)). Thus, progressive consumption of methane could generate a shallower slope of  $\Delta H/\Delta C$  under well conditions reported in [Miller et al. \(2016\)](#), leading to preferential  $\delta^{13}\text{C}$  enrichment.

Diffusion should not be ignored in this system. [Etiopie \(2016\)](#) suggests the gases would be transported via advective flow. However, we are not sampling near a fault contact delivering fluids or gases to the surface. Below 50 meters, the [peridotite aquifer](#) has low permeability ([Dewandel et al., 2005](#)). Fluids are stored over long residence times, and the surface of the unconfined [water table](#) is located a few tens of meters below the land surface ([Paukert, 2014](#)). We can then assume some loss of  $\text{H}_2$  and  $\text{CH}_4$  through diffusive [gas transport](#), but it is important to note that currently, there is not sufficient data to support either diffusive or [advective transport](#). If we consider the isotopic effects derived from the diffusion of  $^{12}\text{CH}_4$ ,  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_3\text{D}$ , independent of oxidation

processes, we would predict a very shallow slope for  $\Delta H/\Delta C$  for diffusive loss of  $CH_4$  alone ([Alperin et al., 1988](#)).

We are currently studying 15 wells in the Samail [ophiolite](#) of Oman that tap into [gabbro](#) and peridotite-hosted subsurface fluids. By capturing [methane](#) from a greater number of geochemical, hydrological and biological conditions, and applying a greater focus on the molecular composition of the full suite of [hydrocarbons](#), we should be able to better unravel the sources of  $CH_4$ , possible mixing of  $CH_4$  sources, and processes that contribute to  $CH_4$  turnover and loss. We are also now working with cultures of methanogenic and methane consuming organisms cultivated from well NSHQ04 in Oman that will permit greater scrutiny of the processes controlling the observed [isotopic composition](#) of  $CH_4$ . The discussion in [Miller et al. \(2016\)](#), [Etiopie \(2016\)](#) and this reply highlight some of the critical processes to be deciphered in the coupling between low-temperature geochemical and biological processes in the  $H_2$  and  $CH_4$  rich fluids commonly found in ophiolites. Although we cannot yet definitively pinpoint the  $CH_4$  origins in the Oman [aquifer](#), it will certainly require further research into both biotic and abiotic processes. We are excited that this work has generated interest in the scientific community, and this debate should continue to fruitfully evolve.

## References

### [Alperin et al., 1988](#)

M.J. Alperin, W.S. Reeburgh, M.J. Whiticar **Carbon and hydrogen isotope fractionation resulting from anaerobic methane oxidation**

Global Biogeochem. Cycles, 2 (1988), pp. 279-288

[CrossRefView Record in Scopus](#)

### [Dewandel et al., 2005](#)

B. Dewandel, P. Lachassagne, F. Boudier, S. Al-Hattali, B. Ladouche, J.-L. Pinault, Z. Al-Suleimani **A conceptual hydrogeological model of ophiolite hard-rock aquifers in Oman based on a multiscale and a multidisciplinary approach**

Hydrogeol. J., 13 (2005), pp. 708-726

[CrossRefView Record in Scopus](#)

### [Etiopie, 2016](#)

G. Etiopie **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), pp. 217-241

[View Record in Scopus](#)

### [Etiopie et al., 2013](#)

G. Etiope, B.L. Ehlmann, M. Schoell **Low temperature production and exhalation of methane from serpentinized rocks on Earth: A potential analog for methane production on Mars**  
Icarus, 224 (2013), pp. 276-285

[ArticleDownload PDFView Record in Scopus](#)

[Etiope and Schoell, 2014](#)

G. Etiope, M. Schoell **Abiotic gas: atypical, but not rare**  
Elements, 10 (2014), pp. 291-296

[CrossRefView Record in Scopus](#)

[Falk and Kelemen, 2015](#)

E.S. Falk, P.B. Kelemen **Geochemistry and petrology of listvenite in the Samail ophiolite, Sultanate of Oman: Complete carbonation of peridotite during ophiolite emplacement**  
Geochim. Cosmochim. Acta, 160 (2015), pp. 70-90

[ArticleDownload PDFView Record in Scopus](#)

[Kelemen et al., 2011](#)

P.B. Kelemen, J. Matter, E.E. Streit, J.F. Rudge, W.B. Curry, J. Blusztajn **Rates and mechanisms of mineral carbonation in peridotite: natural processes and recipes for enhanced, in situ CO<sub>2</sub> capture and storage**

Annu. Rev. Earth Planet. Sci., 39 (2011), pp. 545-576

[CrossRefView Record in Scopus](#)

[Miller et al., 2016](#)

H.M. Miller, J.M. Matter, P. Kelemen, E.T. Ellison, M.E. Conrad, N. Fierer, T. Ruchala, M. Tominaga, A.S. Templeton **Modern water/rock reactions in Oman hyperalkaline peridotite aquifers and implications for microbial habitability**

Geochim. Cosmochim. Acta, 179 (2016), pp. 217-241

[ArticleDownload PDFView Record in Scopus](#)

[Paukert, 2014](#)

A. Paukert **Mineral Carbonation in Mantle Peridotite of the Samail Ophiolite, Oman: Implications for Permanent Geological Carbon Dioxide Capture and Storage**

Columbia University (2014)

Available at: [http://lyly-mac.gps.caltech.edu/ReprintsYLY/A\\_RecentPapers/yung%20chen%202015%20methane-on-mars-2332-2519-1000125.pdf](http://lyly-mac.gps.caltech.edu/ReprintsYLY/A_RecentPapers/yung%20chen%202015%20methane-on-mars-2332-2519-1000125.pdf) [Accessed June 28, 2016]

[Wang et al., 2016](#)

D.T. Wang, P.V. Welander, S. Ono **Fractionation of the methane isotopologues <sup>13</sup>CH<sub>4</sub>, <sup>12</sup>CH<sub>3</sub>D, and <sup>13</sup>CH<sub>3</sub>D during aerobic oxidation of methane by Methylococcus capsulatus (Bath)**

Geochim. Cosmochim. Acta, 192 (2016), pp. 186-202

[ArticleDownload PDFView Record in Scopus](#)

[Weyhenmeyer et al., 2002](#)

C.E. Weyhenmeyer, S.J. Burns, H.N. Waber, P.G. Macumber, A. Matter **Isotope study of moisture sources, recharge areas, and groundwater flow paths within the eastern Batinah coastal plain, Sultanate of Oman**

Water Resour. Res., 38 (2002), p. 1184

1

Co-corresponding author.