

Authors' response to Anonymous Referee #2

R: The Defratyka et al. manuscript describes the distribution of doubly substituted isotopologues in exospheric reservoirs and their relevance in constraining the sources of atmospheric methane. The paper is important in that describes how methane clumped isotopes can potentially help in the quantification of atmospheric sources which are of key importance to atmospheric scientists working to model the source and sink of key greenhouse gases, including methane.

Two challenges to this approach (as described in the introduction) have been the incorrect assignment of kinetic isotope effects in sink reactions, and also assumptions regarding the source signatures (Line 122). In order to correct this, the authors have compiled a database of 1500 previously published clumped isotope results. Because the equilibrium distribution of isotopologues is temperature dependent, the sources can be inferred based upon expected source temperatures, although this also has some caveats (Line 97).

Of the field-sampled sources, thermogenically derived methane is the most common, as has been verified through traditional gas measurements of cold seeps in recent decades (e.g. stable carbon isotopes of methane, methane/ethane ratios, etc.). Similar approaches have been taken to determine biogenic end-member distribution in cold seeps. As Defratyka et al. concede in this manuscript (line 331), abiotic methane is quite poorly constrained. The sources and distribution of abiotic methane are adequately described in this paper (line 405). Nonetheless, the difficulties in ascertaining the abiotic component are not that straightforward, given that the methane concentrations are quite low in high-temperature gases such as those in submarine hydrothermal vents, geothermal wells, and fumeroles. In these cases, CO₂ gas and, in some cases nitrogen gas, are major constituents while methane may only be a couple percent of the total gas content (as opposed to cold seeps where methane often comprises over 90% of the total gas content). As such, abiotic methane derived at high temperatures can easily be contaminated by other sources, such as thermogenic methane gas released during pyrolysis of organic matter in surrounding sediment and, as reviewer, it is of my personal opinion that methane ascribed as being of purely abiotic origin be viewed with some caution.

As described by the authors, the net sink for methane in wetlands and marine systems is either AOM or AeOM. The kinetic isotope effects associated with each process are unique and help distinguish between the two. On the other hand, tropospheric methane removal through OH reduction seems to have only a minimal effect on the remaining CH₄.

This is the most complete compilation of doubly substituted methane isotopologues and the global map of sample distribution covers an impressive global range. Nonetheless, the sample density is patchy (fig. 7) and there are vast areas around the globe that remain unsampled, including some areas of very high methane emission. Given that data is lacking, and sampling is skewed towards some areas more than others, it is possible that further refinements in global sample distribution will change the distribution of clumped isotope results (fig. 5).

All in all, this data description paper is well written and describes the potential for clumped isotope studies to be applied to methane source determination in future studies. As such, I recommend this paper for publication, and also look forward to ongoing work which provides a more complete data set in the future.

A: We thank the reviewer for their review and positive comment. We also value that the difficulties of source attribution and kinetic isotope effects have been highlighted by the reviewer. We are also grateful for mentioning difficulties in detecting abiotic CH₄, particularly in high-temperature

environments, where low methane concentrations and co-emitted gases provide analytical difficulties. It shows potential direction for more detailed field studies of abiotic CH₄. As we discussed in the manuscript, we also see the need of that future dataset extensions to enhance spatial and source coverage. Overall, we are grateful that the reviewer appreciates the current data compilation and they are enthusiastic to see further research of clumped isotopologues of CH₄.