Ms. Ref. No.: OG-5031R1

Title: Incorporation of water-derived hydrogen into methane during artificial maturation of kerogen under hydrothermal conditions Organic Geochemistry

Dear Dr. David T. Wang,

David,

Sorry this has taken so long, but the Joe Curiale, the Associate Editor assigned to this paper, had a very difficult time getting people to agree to be reviewers. This is seems to be a growing problem for all papers.

Reviewers have now commented on your paper. You will see that they are advising that you revise your manuscript. If you are prepared to undertake the work required, I would be pleased to reconsider your revised paper for publication. Reviewer #1 and the Associate Editor have attached files that you need to download from the Editorial Management system.

Authors are normally expected to provide a revised manuscript within 4 weeks. After this time the manuscript will be cleared out of the system and a "revision" after this date would have to be submitted anew and given a new tracking number. Under extenuating circumstances, the Associate Editor should be contacted with a request for an extension. Significantly delayed revisions may become superseded in the literature and require changes beyond those requested by the reviewers and Associate Editor.

For your guidance, reviewers' comments are appended below. Please note that reviewers may have uploaded files as part of the review. If this is the case, you can access the uploaded files on the Editorial Manager.

If you decide to revise the work, please submit a list of changes or a rebuttal against each point raised, a copy of the manuscript with track changes and a clean copy of the manuscript when you submit the revision. Organic Geochemistry also encourages authors to include an acknowledgement of the time and effort provided by the reviewers, whether they are anonymous or have been identified.

Yours sincerely,

Clifford C. Walters, PhD

Editor-in-Chief

Organic Geochemistry

**Dear Editors,**

**We have addressed the comments by the AE and Reviewers below. Please see the attached revised manuscript with tracked changes, as well as a clean copy of the Manuscript. Thank you,**

**David T. Wang on behalf of coauthors.**

**7/13/2022**

Reviewers' comments:

Associate Editor (Joe Curiale)

The original submission of your manuscript, designated OG-5031, was reviewed by Associate Editor Lloyd Snowdon prior to placing the manuscript with peer reviewers. The paper was then returned to you for revisions, which you provided. Upon receipt of the revised version – now designated OG-5031R1 – the Chief Editor placed the paper with me (J A Curiale) to serve as Associate Editor.

Before proceeding any further, let me start with an apology – for how long it has taken to get peer reviews back to you. As you may be aware, finding high-quality peer reviewers – experienced, willing and able – is tough these days; I placed more than 10 review invitations before receiving two acceptances. In the end, though, I believe we now have excellent reviews – reviews which should help you improve the paper.

Your revised version, OG-5031R1, has been reviewed by three individuals: Reviewer 1 (Daniel Dawson), Reviewer 3 (anonymous) and Reviewer 4 (J A Curiale, as Associate Editor) (not sure why a “Reviewer 2” assignment was skipped in Elsevier’s Editorial Manager…). Reviewers 1 and 3 have provided comments below, and Reviewer 1 has also uploaded a marked manuscript for you to download and examine. Reviewer 4 has provided all comments on the paper directly on a marked manuscript uploaded to Editorial Manager, and available to you for download.

Reviewers 1 and 3 have recommended that the paper be “published with minor changes”, and my recommendation as Reviewer 4 is essentially the same. Thus, I am recommending to the Chief Editor that the paper be revised and considered for acceptance have the revisions are examined.

All reviewers’ comments are quite clear, so I will not go over them in detail here. Reviewer 1, in his marked manuscript and his comments below, makes numerous substantive and editorial suggestions, ranging from the need for consistency in units to the need for re-plotting in some cases (and combining figures) to re-wording needed for clarification. Reviewer 3 (all comments provided in detail below) also makes editorial and substantive recommendations, and provides some additional needed references. In my own review, provide on-manuscript in the uploaded file, I have made four substantive remarks as well as several editorial changes directly on the manuscript.

I encourage you to examine the reviews carefully, and hope that you are agreeable to modifying the paper by incorporating the changes recommended by the reviewers; it would certainly be a good addition to the literature, and fits well into Organic Geochemistry. Should you choose to proceed, please return (a) a track-changes version of your revisions, (b) a changes-accepted version, and (c) most importantly, a detailed cover letter describing how you have dealt with each recommendation of each reviewer. I look forward to hearing back from you, and again, apologies for the long turnaround time on this manuscript.

**We appreciate the editors’ efforts to locate expert reviewers and have addressed all comments individually below.**

COMMENTS FROM REVIEWERS 1 AND 3 FOLLOW.

**REVIEWER #1**

Reviewer #1: This manuscript presents the results of an artificial source rock maturation experiment to evaluate the incorporation of water-derived hydrogen into generated methane, and discusses the implications on D/H ratios of generated thermogenic gases and hydrocarbon generation potential.

I commend the authors on submitting an extremely interesting and well written manuscript, having carried out a well conceived and designed artificial maturation experiment. I would also like to commend the authors on not only presenting their interesting experimental results in relation to H/D exchange, but also including useful and insightful commentary on the implications for natural petroleum systems. I believe this will be of significant interest to readers of Organic Geochemistry.

I have no hesitation in recommending this manuscript for publication in Organic Geochemistry, and have suggested only minor changes in the annotated PDF provided with this review. The majority of changes are cosmetic in nature, in order to follow the Organic Geochemistry style guide.

Regards,

Daniel Dawson

**We appreciate Dr. Dawson’s comments and have copied his comments from the uploaded PDF and address them below.**

**Editorial changes are made in the Word document with tracked changes.**

L136: Recommend plotting the initial maturity as a horizontal line on the plot in Figure 1B.

**Now plotted in revised Figure 1B**.

L145: Consider using consistent units (micrmol/kg) to make it easier for the reader, i.e. 1,110 micromol/kg in this case.

**Left as-is.**

L180: Unpublished results

**These are now published; changed to Turner et al. (2022).**

L187: Consider combining Fig. 3 and 4 into a single figure

**Combined into single figure. Fig 3 = new Figure 3A, and Fig 4 = new Figure 3B.**

L210-211: But the source rock matrix is likely important as a catalyst for the exchange of kerogen-bound H with D2O (prior to methane generation) - I think it's important to clarify this point.

**Added as footnote 3: “While it is not an important factor in exchange between CH4 and D2O, the source rock matrix is likely important as a catalyst for the exchange of kerogen-bound H with D2O (prior to methane generation), a process discussed in §3.4.2 and in Alexander et al. (1984).”**

L229-230: This has been well established, recommend replacing "may have" with "have" and including some references (e.g. Schimmelman et al., 2006).

**Done.**

**REVIEWER #3**

Reviewer #3: In this study, the authors have evaluated incorporation of deuterium into C1-C6 gas products generated during closed system pyrolysis of an Eagle Ford shale sample with periodic temperature increases and sampling of a single experimental vessel. The results show that gases generated at low thermal maturities contain mostly hydrogen native to the source kerogen, but deuterium incorporation from the aqueous phase increased with increasing thermal stress. However, the pattern of deuterium incorporation followed a somewhat unexpected progression (i.e., very little CH2D2 relative to other isotopologues). At the highest thermal stress level, the main product was CD4 showing substantial incorporation of aqueous hydrogen isotopes into catagenetic products. This result indicates that estimates of hydrocarbon generating potential from source rocks based on their native hydrogen content may underrepresent their true potential.

The paper is well written and presents findings that will be of great interest to the readers of Organic Geochemistry. The results are consistent with other similar pyrolysis based studies, but the focus on gas isotopologues is somewhat unique, though I refer the authors to another OG paper from Dias et al. that also showed aqueous hydrogen incorporation into generated HC gases from coal. My recommendation is that the article be Accepted after minor revisions.

**We appreciate the Reviewer’s comments and include several of the suggested references in the revised version.**

Suggestions for edits and other comments:

Line 24: change "in" to "with"

**Done.**

Line 64: Dias et al. have evaluated incorporation of aqueous hydrogen into gaseous products during hydrous pyrolysis of coals to differentiate native and generated hydrocarbon gases.

**We appreciate the suggested reference. The Dias et al. study is constructed differently than those cited on Line 64. The ones cited here all used D2O as reactant, whereas the Dias et al. study used local tap water. Nevertheless, it is a study that is consistent with incorporation of water-derived hydrogen into generated thermogenic natural gases. We have added a paragraph-long discussion to the Results and Discussion section (l. 268+):**

**In a differently-constructed study, Dias et al. (2014) evaluated incorporation of aqueous hydrogen into gaseous products during hydrous pyrolysis of bituminous coal samples taken from the same coal seam along a transect at various distances away from an igneous intrusion (and hence with different initial *R*o values ranging from 0.5 to 6.8%). After hydrous pyrolysis, measured *R*o values ranged from 1.4 to 6.9%. An observed dependence of δD of CH4 to δD of water allowed them to differentiate native (sorbed or trapped) and newly-generated (via hydrous pyrolysis) hydrocarbon gases, with almost all (>90%) of CH4 generated from coals with initial *R*o < 2.0% being of newly-generated origin. While the design of their experiment did not allow for quantification of the fractional contribution of water-derived H to the hydrogen content (and hence cannot be plotted on Fig. 5A), their results are consistent with incorporation of aqueous hydrogen into hydrocarbon gases generated by maturation of thermally-immature organic matter.**

Line 68: spell out "WHOI" on first use.

**Changed.**

Lines 82-85: Not sure this digression on H/C ratio of the decalcified and extracted sample is relevant.

**We left this in as it gives context to the H/C ratio of the powdered source rock being elevated relative to isolated kerogen.**

Line 191: Insert "it" after "While".

**Done.**

Line 233: consider changing ""skipped"" to "bypassed".

**Done.**

Line 382: How would you go about estimating the amount of additional natural gas generated by incorporation of aqueous hydrogen and what kerogen structural features do you think would be most relevant to this?

**Very good question. Deuterous pyrolysis or similarly constructed experiments may shed light on ultimate yields in the presence of exogenous H donors. We also expand on the use of more sophisticated chemical kinetic simulations in l. 401-416:**

**Chemical kinetic models employed in the upstream oil and gas industry for exploration purposes invariably use simple, pseudo-first-order reactions. Many parallel reactions may be simulated at once to simulate different classes of kerogen or petroleum breakdown products; however, all reactions are, without exception, pseudo-first-order in the mass of remaining precursor. However, as noted in Xie et al. (2022), the rate coefficients of these notionally unimolecular reactions can be pressure-dependent, because a third-body collision may be required to remove excess energy from the excited intermediates. Therefore, an algorithmic reaction mechanism generator (RMG; Allen et al., 2012)—operating from a database of elementary reaction kinetics—may be used to determine the important reactions involved in the breakdown of kerogen and petroleum, and to estimate their rate coefficients under typical subsurface pressure & temperature conditions in active source rocks. Furthermore, water is almost invariably excluded as a reactant from computational studies of the thermal decomposition of organic matter because of the computational burden involved. Examples include Class (2015) and Gao (2016) wherein geological oil-to-gas cracking was studied by using RMG to simulate individual radical reactions involved in the pyrolysis of model organic compounds under dry (water-absent) conditions. Very recent developments in RMG now allow it to handle gas- and liquid-phase heterogeneous reactions (Liu et al., 2021). In the future it may therefore be possible to extend the aforementioned studies on pyrolysis of model compounds to include H­2O as a reactant.**

**As for kerogen structural features, that is beyond the scope of this work, but has been covered in various articles on AFM-IR, such as Jubb et al. (2019).**

Line 420: Bern et al. have estimated water-rock ratios for shales in natural settings and found that they are several orders of magnitude lower than what is typically used in experimental shale studies.

**Thanks for the reference. Added as Line 424,** “**By contrast, water:rock ratios for shales existing in nature (0.003:1 to 0.23:1; Bern et al., 2021) are several orders of magnitude lower than those used in experiments.”**

Line 432: Referring back to my comment on Line 382, I think if you were to do similar experiments on a variety of immature kerogen isolates from different environments and containing OM from different sources that were well characterized (NMR, FTIR, XPS, etc.) this could be determined. Kelemen et al. present a range of kerogen types and spectroscopic properties that could perhaps be used in a modeling study incorporating kerogen structural modeling and simulated hydrous pyrolysis conditions.

**Indeed. This is an ExxonMobil (New Jersey lab) study that is an offshoot of the same project from which CS-CYM came. Unfortunately, to my (DTW’s) knowledge this kind of work is no longer done at ExxonMobil. It will have to be followed up elsewhere.**

**REVIEWER #4**

Reviewer #4: This document contains all review comments by J A Curiale on the manuscript (Wang et al.) “Incorporation of water-derived hydrogen into methane…”. Changes to the text are made in lower case on the manuscript; comments to the authors are made in UPPER CASE on the manuscript and in the numbered list below.

This paper concerns the presence of deuterium in methane generated during hydrous pyrolysis of extracted Eagle Ford rock in a D2O-rich environment, and interpretations of methane origin based on results. It adds weight to the idea that water in the petroleum system is, indeed, a critical element in natural gas generation. The paper is well-written and well-reasoned, and should be published after incorporating the minor comments suggested below as well as those of peer reviewers.

**We thank Dr Curiale for his comments and have incorporated them into the revised manuscript.**

1. The experiment described here was conducted on a solvent-extracted rock sample. However, the authors sometimes refer (in the text) to changes occurring in kerogen. Because ‘kerogen’ is, in many ways, a laboratory-created product (concentrated insoluble organic matter), I recommend that instead of referring to the experimental material as ‘kerogen’ it should be referred to as ‘extracted rock’. Indeed, it’s possible (likely?) that using actual kerogen rather than extracted rock in this experiment would have yielded different results. [It is also interesting to speculate on how your results may have differed if you had used crushed-but-not-powdered extracted rock for the experiment. As you infer a few paragraphs before your Conclusions section, a mono-layer of water on clay particles could have had a significant effect. Indeed, it may have been the origin of dominantly undeuterated methane in the early stages of the experiment.]

**We have replaced or clarified a number of instances where the word ‘kerogen’ is used to refer to the solvent-extracted rock powder. It now appears as “powdered solvent-extracted source rock” or some variant of this, to prevent confusion with a *kerogen isolate*. We have retained the use of the term “kerogen” in its meaning as ‘high-molecular weight, insoluble sedimentary organic matter’. Where appropriate, we have specified the presence of additional types of organic matter, for example: “kerogen and bitumen (or petroleum) maturation”.**

**We have also changed the title of the manuscript to: “Incorporation of water-derived hydrogen into methane during artificial maturation of source rock under hydrothermal conditions”**

**We added the point about residual water contributing to undeuterated methane in lines 441-444:**

**A residual water monolayer on clay particles, if present, might be responsible for some of the undeuterated methane in the early stages of our experiment. If this is the case, using crushed rock instead of rock powder in the experiment might yield yet higher proportions of C1H4 in the earlier samples.**

1. The presence of ethylene and propylene in the experimental measurement at 200C is curious – makes me wonder if these are, at least to some extent, indigenous (occluded; adsorbed) in the extracted rock from the start, rather than generated thermally in the experiment. In footnote 3, the authors note (and discount) the analogous possibility involving methane. The measurable content of EOM recovered from solvent extraction of lab-prepped kerogen, which has already been solvent-extracted to generate the extracted rock from which the kerogen is prepared via acid treatment, suggests the inefficiency of a single round of solvent extraction of the starting rock.

**It is possible that ethylene and propylene could be partially indigenous. We now note this in l. 163-165:** **“Some portion of the ~10−6.5 mol/kg of these alkenes present at time point #1 could have been indigenous to the source rock (i.e., adsorbed and leached out during initial heating).”**

1. A “blank run” (see authors’ footnote 4) would have served to address the water-methane exchange question as well as other issues (I have a vague memory that Tom Hoering tried something like this many years ago).

**Yes, though this is somewhat unnecessary now given new experimental data from Turner et al. (2022) directly measuring the rate of isotopic exchange between CH4 and H2O (it is slow and insignificant relative to lab experiment timescales).**

1. In section 3.4.3 the authors suggest that CH4 is isotopically frozen in conventional reservoirs, given that these reservoirs are commonly at temperatures less than the source rock generation temperature. However, they appear to contrast this situation with that of unconventional reservoirs (source-rock reservoirs). Such a distinction is hard to support, though, because most commercial source-rock reservoir systems are not at maximal burial depths, indicating that generation temperatures in these systems, as for “conventionals”, are still greater than present-day reservoir temperatures.

**This point requires elaboration. It is important to consider that the *cooling rate* has a substantial effect on closure temperatures of CH4-H2O isotopic exchange. In conventional petroleum systems where migration occurs soon after generation, “quenching” of the exchange reaction will likely occur once the temperature of the migrating fluid drops below ~170 C, because migration is likely to occur to a shallower, cooler trap within a short period of time (<0.2 Myr per Jung et al., 2018, implying a cooling rate of ~250 °C/Myr or faster). A minimum, conservative estimate of the cooling rate during migration is 50 °C/Myr (5x slower than Jung et al.). We constructed a model to simulate the cooling of a migrating natural gas as it travels from a hot source rock to a cooler, conventional reservoir using this cooling rate. The model results are shown in Fig. 8A and are reproduced below.**

**We also performed a similar simulation using a cooling rate of 0.5 °C/Myr, which is approximates the thermal regime experienced by source-rock reservoir that has reached maximum burial and is cooling gradually (Fig. 8B). With the longer exposure time (millions of years) a methane molecule trapped within a source-rock reservoir can remain between 160 and 130 °C, substantially more exchange is expected to occur.**

**We have added this discussion in l. 356-362, 375-378, and footnote 7, and reference the new Figure 8.**

