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EARTH AND ENVIRONMENTAL SCIENCE
REPLICATION

Potential analytical interferences when measuring Tmax during temperature programmed pyrolysis of hydrothermally altered volcanoclastic sediment

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Abstract
The temperature of maximum pyrolysis yield (known as Tmax) can be used to determine the level of thermal alteration in sedimentary organic matter; higher Tmax values represent higher thermal alteration. Tmax is commonly measured on petroleum source rocks or similar sediments with high organic carbon contents. It would be desirable to measure the Tmax of volcanic sediments because they can have complex patterns of thermal alteration. However, volcanic sediments often have low total organic carbon contents and consequently are susceptible to analytical interferences. Despite this, it can be shown that meaningful Tmax measurements can still be made in sediment with organic carbon contents as low as 0.2% and that interference caused by bitumen or ionizable salts can be mitigated by solvent extraction and rinsing with water. Thus, it is reasonable to use temperature programmed pyrolysis to assess levels of thermal alteration in even low total organic carbon volcanoclastic sediments.

Key words: Rock-Eval; temperature programmed pyrolysis; thermal maturity; Tmax; volcanic sediment

Introduction

Temperature programmed pyrolysis, often called "Rock-Eval" after the trade name of a related analytical instrument, rapidly characterizes types of organic carbon in soil, sediments, and rocks and the potential for petroleum to be generated from source rocks. The assay returns information on the proportion of volatile and involatile organic carbon and thermal recalcitrance in terms of pyrolyzable and combustible organic matter (Espitalié et al., 1977). During temperature programmed pyrolysis, sediments are heated so that initially only volatile components evaporate, prior to the onset of temperatures at which larger organic materials thermally decompose (pyrolyze) and generate newly formed volatile organic compounds (Espitalié et al., 1977; Peters, 1986). Products of these two stages are quantified, and the temperature at which the highest yield of compounds is obtained is recorded (the Tmax parameter). Additional combustive stages can be used to assay the non-pyrolyzable component (Baudin et al., 2015).

Objective

Volcanic calderas are not a setting to which Rock-Eval has been commonly applied. Nonetheless, using Tmax to assess the level of thermal alteration of sediments deposited in volcanic calderas is potentially

Table 1. Sample description, TOC, Tmax, and yields (S1 and S2) for hydrothermally altered volcanic sediment prepared by different methods

Sample	Depth mbsf	Geological notes	Downhole temp °C	Leco TOC %	RE TOC %	Crushed Tmax °C	Solvent-cleaned Tmax °C	Water-rinsed Tmax °C
IODP 331, C0013C 1H-12, 78–79 cm	9.1	Hydrothermally altered volcanoclastic sediment (devitrified)	~150	0.62	0.87	313	422.5	409.5
IODP 331, C0014B 4H-cc, 13–15 cm	35		~125	0.11	0.15	417	418.5	407
IODP 331, C0013C 1H-cc, 004–005 cm	12.6		~150	0.01	0.04	425	397	406

Abbreviations: Crushed Tmax, Tmax for crushed samples; Downhole temp, present day temperature of samples in volcanic caldera; Leco TOC, TOC measured by combustive technique using an instrument more sensitive to low-carbon-content materials; mbsf, meters beneath seafloor; RE TOC, TOC returned by Rock-Eval; Solvent-cleaned Tmax, Tmax for solvent-rinsed samples; TOC, total organic carbon; Water-rinsed Tmax, Tmax for samples rinsed by water.

very useful as it can provide information on prior periods of volcanic activity related to both volcanism and hydrothermal activity. However, measuring Tmax may be complicated in a caldera setting because sediments are organic lean in terms of low total organic carbon (TOC) and also pyrolysis yield (in Rock-Eval, the pyrolysis yield is termed the S2 peak), and thus the potential for analytical interferences is high in organic-lean volcanic sediments (Espitalié et al., 1984). Furthermore, hydrothermal fluids mobilize bitumen (Simoneit & Lonsdale, 1982) and precipitate ionizable salts in the form of hydrothermal minerals, both of which are known as analytical interferences (Baudin et al., 2015; Peters, 1986). Therefore, the objective of this study is to determine the minimum TOC or organic leanness of a sample of volcanic sediment that might still be used to measure Tmax, and if currently known sample-processing techniques (Baudin et al., 2015) can mitigate analytical interferences when measuring Tmax in samples collected from volcanic calderas with hydrothermal activity.

Methods

Samples

Samples (Table 1) of hydrothermally altered volcanic sediment are from a subseafloor hydrothermal system hosted within a subsea volcanic caldera and were collected during Integrated Ocean Discovery Program (IODP) Expedition 331 from Iheya Knoll, offshore Okinawa, Japan (Takai et al., 2011). All samples are a variable mixture of devitrified volcanic ash and hemipelagic mud, a low and high TOC lithology, respectively. Relative to the loci of the present-day hydrothermal vent, previous work (Yeats et al., 2017) has shown that distinctions can be made between (a) sediment close to venting hydrothermal fluids that contains hydrothermal mineral assemblages, (b) sediment with a lesser hydrothermal mineral content distal from the vent, and (c) sediment with no significant hydrothermal mineral content but still within the hydrothermal field. Samples for this study have hydrothermal mineral content but are some distance from venting hydrothermal fluids. Further information about samples is in Table 1, and the expedition is described in Takai et al. (2011).

Sample processing

Dry samples of sediment cores were processed by one of three methods: (a) disaggregation using a pestle and mortar, a standard preparative procedure, (b) disaggregation and soxhlet extraction for 48 hr using a

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mixture of 97:3 v/v dichloromethane:methanol, removes petroleum and bitumen, (c) disaggregation, solvent extraction, and rinsing with deionized water, and a 50:50 v/v solution of ethanol:deionized water (ratio of 5:1 v/v water to sediment), removes interfering ionizable salts such as halite and anhydrite.

Rock-Eval 6

The Rock-Eval pyrolysis method used was the basic analysis cycle for Rock-Eval 6: in brief, an isothermal stage (300°C) is followed by a pyrolysis stage in which temperature rises from 300 to 650°C at 25°C/min (Behar et al., 2001). All analyses were performed in duplicate, with duplicate standards (IFP 160000) analyzed every six to eight samples. Rock-Eval results are presented in Table 1. The main output from this procedure is a record of yield for a given temperature and experimental time. A plot of pyrolysis yield versus time is called a pyrogram, and these are presented in Figures 1 and 2.

Results

Signal denudation due to the organic carbon leanness of volcanic samples was assessed by analyzing varying amounts of standard. It can be seen (Figure 1a) that when quantities are reduced by a factor of 10 from the typical quantities analyzed (TOC of 1.25 to 0.66 and S2 of 4.48 to 0.97 mg/g sed), little change in Tmax is produced and the signal measured is orders of magnitude above a procedural blank. Within a pyrogram, errors in the determination of Tmax can result when a maximum is not easily determined because of the low curvature of peaks or the presence of interfering peaks generated as analytical artifact. Despite Figure 1a implying a reduction in curvature with TOC, this is not the case when data are rescaled (Figure 1b) and Tmax can be reliably measured for a TOC as low as 0.34%. Even for a TOC of 0.02%, the Tmax would be expected to be within measurement error. Only for extremely low quantities of organic carbon would analytical interference produce a background signal that prevents the measurement of Tmax, as any signal ~20 times above a blank would be expected to yield meaningful Tmax measurements. Therefore, although matrix effects may cause quantitative parameters based on pyrolysis yields to be underestimated (Espitalié et al., 1984; Landford & Blanc-Valleron, 1990), a low quantity of analyte need not prevent the measurement of Tmax in low-TOC volcanoclastic sediment. Instead, the main interference with the measurement of TOC in volcanoclastic sediments is likely to be exogenous compounds introduced by hydrothermal systems.

In Figure 2a, the dominant peaks at low or sub-pyrolysis temperatures (~320°C) are caused by exogenous bitumen. In the solvent-extracted samples, the low-temperature peaks are absent and the dominant peaks are centered at 410–423°C. It is important to note that bitumen can be both volatilizable and involatile and that involatile bitumen pyrolyzes at higher temperatures similar to kerogen (e.g., Gilsonite has a Tmax > 450°C; Peters, 1986). Bitumen has been reported in many hydrothermal systems where the hot fluids can both generate and transport it (Simoneit & Lonsdale, 1982). Previous work has detected petroleum residues in samples from Iheya Knoll (Bowden et al., 2016).

Parasitic ionization of salts generates peaks in the 480–550°C region of pyrograms due to the thermal decomposition of salts comprising lighter elements (Baudin et al., 2015), and such a feature can be seen for the non-rinsed samples in Figure 2b,c as a peak at ~515°C. These peaks are not prominent in samples that have been rinsed and solvent-extracted. Figure 2b,c corresponds to samples from horizons where anhydrite, barite, and other hydrothermal mineralization is present (Takai et al., 2011). Relative to other cases presented in the literature, the peaks for ionizable salt in Figure 2b,c are large in comparison with the main pyrolysis peaks. This is a consequence of the low TOC and thermal maturity of the pyrolyzed and hemipelagic sediment (<0.5% TOC), which permits an easy visual distinction to be made between peaks for pyrolyzed kerogen at ~420°C and the higher temperature peaks due to ionization of soluble salts (>480°C). Being able to be certain that the peak at ~515°C is not from thermally mature organic matter is important in this case, as otherwise such a peak might be taken

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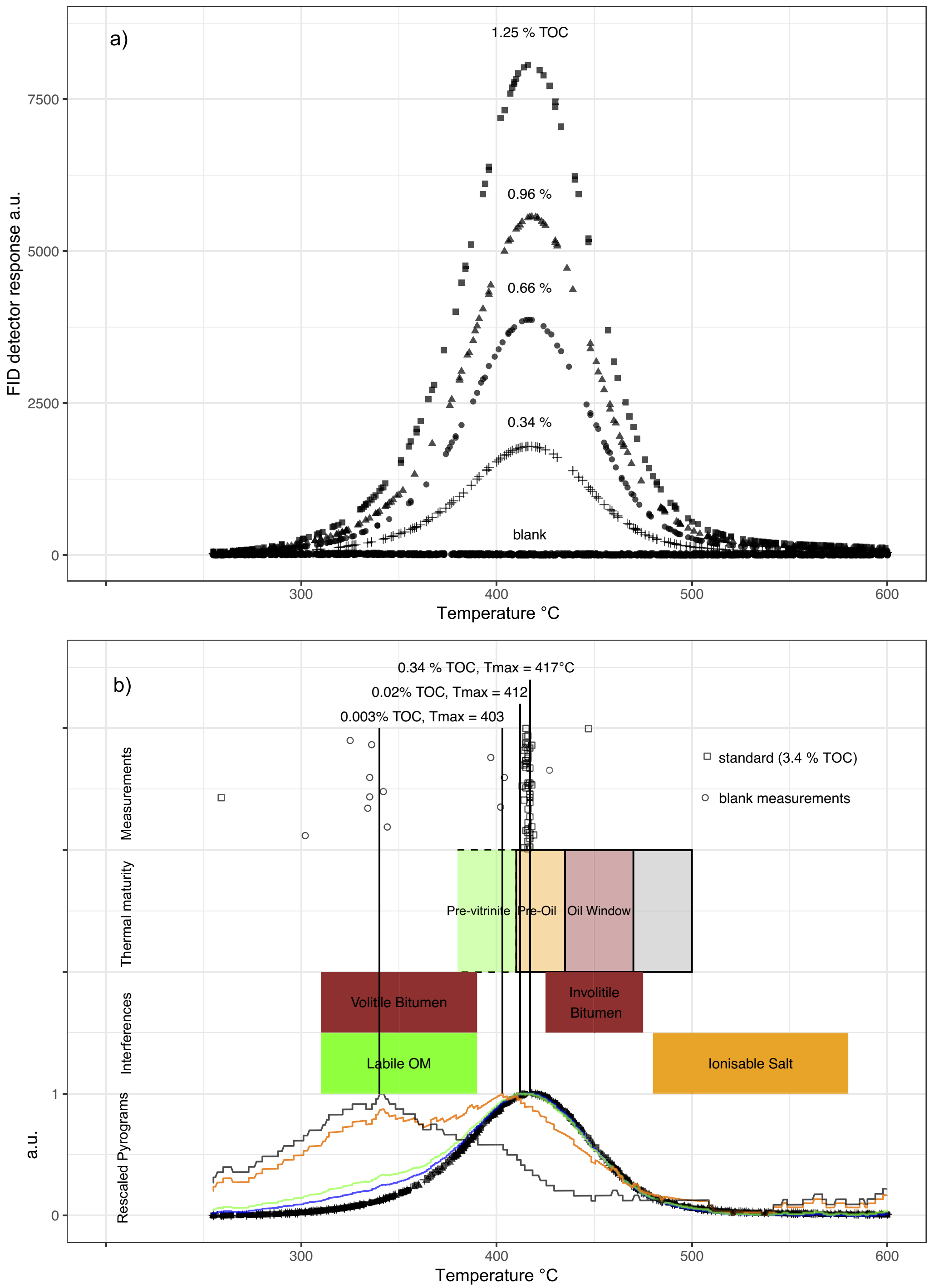

Figure 1. Pyrograms that illustrate the sensitivity Tmax to total organic carbon (TOC). (a) Flame ionization detector responses for different quantities of organic carbon. Note that when plotted this way procedural blanks produce a very weak signal. Most sediments investigated for petroleum source rock potential would be expected to have a TOC of >0.5%. (b) Points of reference for determining the utility of Tmax measurements; repeat measurements of standard with a Tmax of 417°C, repeat blank measurements, and the points of reference for significant differences in terms of thermal maturity and regions effected by know analytical interferences discussed in text. Bottom of (b) are data from (a) rescaled from 0 to 1, with pyrograms calculated for the very low TOC found in hydrothermally altered volcanic sediment.

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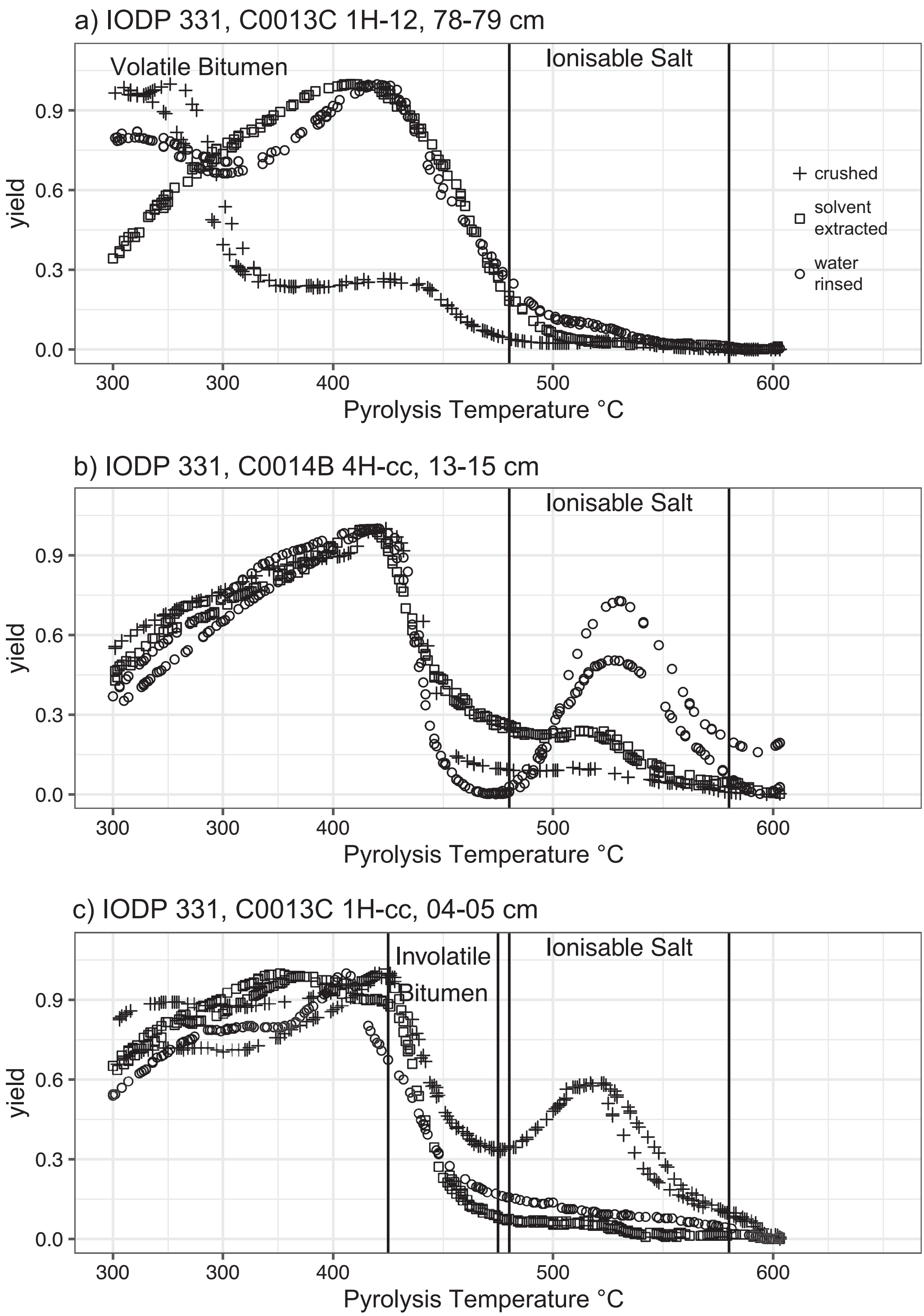

Figure 2. Pyrograms of hydrothermally altered volcanic sediment that illustrate the consequences of analytical interferences by (a) IODP 331, C0013C 1H-12, 78–79 cm—effected by bitumen, (b) IODP 331, C0014B 4H-cc, 13–15 cm—affected by ionizable salts, and (c) IODP 331, C0013C 1H-cc, 004–005 cm—sample with a low TOC and effected by bitumen and ionizable salt. Note that the initial stage is isothermal at 300°C, thus 300°C appears successively on the x-axis in the early part of the pyrogram.

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as evidence that some of the organic carbon in the sample had experienced a very high level of thermal alteration (Holtvoeth et al., 2001).

Discussions

Low TOC and organic leanness (TOC 0.5–0.05%) is unlikely to prevent the measurement of Tmax in volcanoclastic sediment. Despite this, as an additional control, blank analyses can be performed, and measurements that do not have a pyrolysis yield (determined by the detector response rather than S2 yield) greater than 20 times the procedural blank were rejected. Based on previous work in other sedimentary settings, it might be expected that ionizable salts and bitumen could interfere with the measurement of Tmax in hydrothermally altered volcanic sediment, and the results presented here show this to be the case. However, currently known sample-processing methods developed in other contexts can be used to mitigate the problem. It is interesting to note that in this study, ionizable salts only marginally raised Tmax because the organic matter had a low thermal maturity; thus, peaks were easily resolved and did not interfere. Conversely, bitumen, depending on whether it is volatile or involatile, might raise or lower the Tmax of pre-oil window organic matter. In low-TOC hydrothermally altered volcanic sediments, bitumen is the more likely analytical interference. As these aspects will vary between and within volcanic basins, further study is needed to understand how temperature programmed pyrolysis can be applied to organic geochemical analysis in volcanic sediments.

Conclusions

The temperature of maximum pyrolysis yield (T_{max}) can be measured in organic lean (TOC 0.05–0.5%) hydrothermally altered volcanoclastic sediment, and these measurements can be used to gauge thermal maturity providing that analytical interferences from instruments and methods, mobile bitumen phases and ionizable salts are considered and if necessary mitigated.

Open peer review. To view the open peer review materials for this article, please visit http://doi.org/10.1017/exp.2023.3.

Data availability statement. Data are available in the manuscript.

Authorship contributions. S.A.B. and Y.Y. conceived the work and wrote the manuscript. S.A.B., Y.K., O.E.O., and M.-Y.T. processed or analyzed the samples. O.E.O. performed the Leco analyses. All Authors contributed to revising the manuscript.

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Conflict of interest. The authors declare no conflict of interest.

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Peer Reviews

Reviewing editor: Dr. M. Satish-Kumar
Niigata University, Niigata, Japan, 950-2181

Minor revisions requested.

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Review 1: Potential analytical interferences when measuring Tmax during temperature programmed pyrolysis of hydrothermally altered volcanoclastic sediment

Reviewer: Paolo Martizzi

Akita University, International Resources

Date of review: 04 December 2022

Conflict of interest statement. Reviewer declares none

Comment

Comments to the Author: This article is showing an interesting application of the Rock-Eval pyrolysis on hydrothermally altered volcanoclastic sediments and discusses concretely the reliability of the results and potential pitfalls related to the inclusion of bitumen and ionisable salts. I have some suggestions that I hope the authors will consider when revising this manuscript:

1. Lines 30 to 36: I think that some reference/s should be added at the end of this sentence;
2. Lines 55 to 57: I think the authors should add a reference figure to the manuscript showing the location of IODP 331 (modified from Takai et al., 2011) to understand the geographical context of the samples;
3. Lines 76 to 78: Please add a reference for the Rock-eval pyrolysis cycle (ex. Behar et al., 2001);
4. In Table 1 and the Results section, the authors did not report/mention the S2 peak value which I believe is very important to understand the precision in the Tmax values. I suggest revising this section by including also a discussion of the S2 peaks values in the different samples;
5. Question: Is there a relationship between the proportion of devitrified volcanic ash and hemipelagic mud and the Tmax? I think it would an important point to add in the Results;
5. In the Conclusions section, the authors should include a sentence that suggests the necessity of further studies to improve the applicability of the method in other volcanoclastic deposits.

Score Card

Presentation

4.7 /5

Is the article written in clear and proper English? (30%)	5/5
Is the data presented in the most useful manner? (40%)	5/5
Does the paper cite relevant and related articles appropriately? (30%)	4/5

Context

4.8 /5

Does the title suitably represent the article? (25%)	5/5
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Does the introduction give appropriate context? (25%)	4/5
Is the objective of the experiment clearly defined? (25%)	5/5

Analysis

4.4 /5

Does the discussion adequately interpret the results presented? (40%)	4/5
Is the conclusion consistent with the results and discussion? (40%)	5/5
Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)	4/5

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Review 2: Potential analytical interferences when measuring Tmax during temperature programmed pyrolysis of hydrothermally altered volcanoclastic sediment

Reviewer: Ayad Faqi-Nori

Soran University, Petroleum Geosciences

Date of review: 10 December 2022

Conflict of interest statement. Reviewer declares none.

Comment

Comments to the Author:

- The authors provided reasonable data and interpretation to achieve the goal of their study. The method section was clear and many parameters have been used in this study.
- The authors are recommended to evaluate the level of the thermal maturity for studied samples using thermal maturity related-biomarkers parameters in the future study if they are willing to do. The extracted organic matter (bitumen) of collected samples can be used for this purpose.
- Technically, 1)the abbreviations cannot be used in the abstract unless they are defined clearly. For example Total Organic Carbon (TOC).

2) Usually there is a hyphen (-) between Rock and Eval. Rock-Eval

- The reference ''Peters, K., Walters, C., & Moldowan, J. (2004). The Biomarker Guide (2nd ed.). Cambridge: Cambridge University Press" is not found in the main body of MS.

Score Card

Presentation

5.0 /5

Is the article written in clear and proper English? (30%)	5/5
Is the data presented in the most useful manner? (40%)	5/5
Does the paper cite relevant and related articles appropriately? (30%)	5/5

Context

4.5 /5

Does the title suitably represent the article? (25%)	5/5
Does the abstract correctly embody the content of the article? (25%)	4/5
Does the introduction give appropriate context? (25%)	4/5
Is the objective of the experiment clearly defined? (25%)	5/5

Analysis

4.8 /5

Does the discussion adequately interpret the results presented? (40%)	5/5
Is the conclusion consistent with the results and discussion? (40%)	5/5
Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)	4/5

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