

Solid Earth Discuss., referee comment RC1
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Comment on se-2021-70

Aaron Jubb (Referee)

Referee comment on "Raman spectroscopy in thrust-stacked carbonates: an investigation of spectral parameters with implications for temperature calculations in strained samples" by Lauren Kedar et al., Solid Earth Discuss., <https://doi.org/10.5194/se-2021-70-RC1>, 2021

In this manuscript, Kedar and co-workers attempt to examine the impact of organic matter deformation from faults and shear zones on determined temperatures from Raman organic matter geothermometers. This is an important and exciting field of study and is certainly worthy of careful investigation. The samples chosen here should be appropriate to evaluate the question 'Does tectonic strain/deformation impact calculated Raman temperatures?' and I was excited to read how the authors carried out this work. Unfortunately, there are some major issues with how this study was executed that hinder the interpretability of the data. Crucially, the empirical geothermometers used to calculate sample temperatures were not applied correctly. To apply these geothermometers correctly, sample Raman spectra must be collected and then analyzed in the same fashion as the Raman spectra that underpin the geothermometers. Because this was not done here, none of the temperature data presented by Kedar and co-workers can be trusted. This concern and other major issues and minor suggestions are detailed below. My recommendation is that major revisions are needed before this work is appropriate to publish and I would be happy to review a revision should the authors decide to pursue that option.

Recommendation: Major revisions

Aaron M. Jubb, Ph.D.

United States Geological Survey

Major Revisions

1. Geothermometers were not applied correctly. Specific problems with each detailed below.

a. Lahfid thermometer: $T = (RA1 - 0.3758) / 0.0008$, here $RA1 = (D1 + D4) / (D1 + D2 + D3 + D4 + G)$ using peak areas from Lorentzian peaks fit to Raman spectra collected with 514 nm laser. To apply this thermometer correctly you need to:

(i) Collect the Raman data with a 514 nm laser because dispersion of the D peak will change the calculated area. See the following references for discussions on dispersion effects on Raman spectra of geologic organic matter:

Lünsdorf, 2016, Raman spectroscopy of dispersed vitrinite – Methodical aspects and correlation with reflectance, *Inter. J. Coal Geol.*, 153, 75-86.

Sauerer et al., 2017, Fast and accurate shale maturity determination by Raman spectroscopy measurement with minimal sample preparation, *Inter. J. Coal Geol.*, 173, 150-157

Jubb et al., 2018, High microscale variability in Raman thermal maturity estimates from shale organic matter, *Inter. J. Coal Geol.*, 199, 1-9

(ii) Fit the collected Raman data using a sum of Lorentzian profiles as Lahfid did, not the pseudo-Voigt profile that was used here.

(iii) Fit the collected Raman spectra with five peaks, not two.

b. Kouketsu thermometer: $T = -2.15(D1 - FWHM) + 478$, collected with 532nm laser, fit using pseudo-Voigt profiles.

The number of peaks fit to the Raman spectra for the Kouketsu thermometer was dependent on several qualitative and quantitative parameters. See flowchart (Figure 3) from Kouketsu 2014 here:

For the sample temperatures in this study (left end of the flow chart), either 4 or 5 peaks needed to be fit to the Raman data in order to correctly apply this geothermometer.

c. Schito and Corrado estimation of VRo% for use in the Barker and Pawlewicz geothermometer: $T = (\ln(\text{VRo}\%) + 1.68) / 0.0124$.

Here the authors have correctly used relationships from Schito and Corrado to determine an equivalent vitrinite reflectance (VRo%) from the Raman spectra. This parameter is then used to determine a temperature using the 1986 thermometer proposed by Barker and Pawlewicz. However, the data that this thermometer is based on are highly uncertain (see Figure 1 from Barker and Pawlewicz 1986 below), making it semi-quantitative at best. Certainly, correlating vitrinite reflectance to an absolute temperature is a large challenge for the field and one that warrants careful study in its own right. Regardless, for the work reported here, an estimation of uncertainty in the determined temperatures using the Barker and Pawlewicz equation **must** be included if this geothermometer is to be used.

2. Analytical uncertainties need to be added to Figures 5, 6, & 7 (where appropriate) and better discussed throughout the text. Specifically, what do uncertainties represent (e.g., propagated precision from fits, standard deviations, reported uncertainties from original geothermometers?), what confidence interval do these uncertainties represent, and what the uncertainties mean for the interpretations drawn from the data.

3. More detail is needed on the organic matter comprising the samples and on the Raman analyses. Specifically:

a. What types of organic matter made up the extracted kerogen? Different organic matter types will have different Raman response due to differences in their molecular structures.

b. How does the kerogen isolation procedure change the Raman response? If this wasn't tested, some text describing why this procedure isn't anticipated to impact the Raman spectra needs to be included.

c. What mesh size were the samples powdered to prior to demineralization?

d. What grade of HCl and at what temperature was used in the demineralization procedure?

e. Were there entrained clay particles in the kerogen isolates that remained after demineralization? If so, could that impact your results?

f. What evidence do you have that graphitization has not occurred in any of your samples?

g. How did you assess the presence/absence of thermal alteration from the excitation laser during Raman collection?

h. What microscope objective was used? What was the numerical aperture? What was the laser polarization?

i. What function was used to smooth the data? How did smoothing the data impact the Raman parameters from the fits?

4. Figure 4 shows 'typical' changes in Raman parameters vs. temperature and strain. However, no discussion (or very little) is given to how these 'typical' trends were determined, especially for temperature. A better representation of this kind of analysis can be seen in Henry et al., 2019, Earth-Sci. Reviews. I recommend removing this figure (at least with regards to temperature) and directing readers to the trends shown Henry et al.

5. The discussion of the Raman band separation (RBS) parameter is unclear throughout and is incorrect in several places. Specifically:

a. Section 5.2: "...RBS appears to show no consistent pattern throughout the stratigraphy...". To me, the RBS parameter shows a consistent, if weak, trend decreasing with depth.

b. Section 5.2: $\pm 4 \text{ cm}^{-1}$ for the RBS parameter is referred to as "high error". What does this error represent (see comment #3) and furthermore, this degree of uncertainty is $< \pm 2\%$ the determined value. Why do the authors think this level of error is high?

c. Section 7.2: The statement "It is possible that the samples in this study are not of high enough maturity for a trend in RBS to be seen...." is not correct. Relatively low temperature organic matter show trends in RBS. In fact, both of the citations provided to support this statement show RBS data with trends for low temperature source rocks. I do not understand where this statement comes from.

d. Section 7.2: The statement "This suggests that frictional heating does not play a significant role in changing the Raman spectral parameters on thrust planes." is not supported by the data. RBS is calculated from D- and G-peak frequency. FWHM and peak height are other Raman parameters not included in the RBS parameter.

6. Line 372: "...we only observe a decrease in FWHM[d], whilst FWHM[g] changes very little...". This suggests that something weird is going on with either the samples or the analysis as this observation is fairly unexpected. More discussion is needed to explore this observation as FWHM[g] is usually considered one of the "best" indicators of maturity in Raman geothermometry.

7. Section 7.8: The statements "From our observations....equation is less effected by strained environments than..." and "The Kouketsu equation is also more suited to strained environments." illustrate a real disconnect in the author's perspective on Raman geothermometers and what is *actually* being measured when you probe organic matter with a Raman instrument. The Raman response from organic matter is dictated by the molecular structure of the organic matter ensemble in the probe volume of the Raman microscope. Raman geothermometers work because the thermal alteration of organic matter structure as it reacts toward a graphite endmember is deemed irreversible. The interesting question this study is trying to ask is "Does strain, independent of temperature, change organic matter structure such that these effects need to be accounted for when determining a temperature from Raman spectra of geologic organic matter?". That is, all Raman geothermometers should be affected by strained environments if strain is changing the molecular structure of the probed organic matter. Stating that one geothermometer is more appropriate than another for strained environs

misses this point. I strongly suggest reworking the discussion and conclusion with perspective on this point.

8. Finally, some discussion should be given to the work examining the Raman response of kerogen to high pressures in laboratory settings. Certainly, the rate of strain between natural samples (as examined here) and laboratory strained samples will be different, but I believe that prior laboratory experiments can provide much insight into the processes under study here. Start with:

Huang et al., 2010, In situ Raman spectroscopy on kerogen at high temperatures and high pressures, *Phys. Chem. Minerals*, 37, 593-600.

Minor Revisions

- Line 30: define "reliable". This word is subjective without context.
- Line 40: The use of the term "organic carbon nanostructure" is misleading. Raman spectroscopy of complex geologic organic matter typically only reports on the aromatic character of the organics due to resonance effects (i.e., the electronic bandgap of the aromatic moieties matches the energy of visible wavelengths commonly used as Raman excitation sources which pumps the response from these functional groups). Suggest rewording as "organic matter aromaticity".
- Line 44: Define "FWHM" at first usage.
- Line 154: Define "BRGM" at first usage.
- Line 171: The statement "Raman spectroscopy measures the wavelengths of backscattered..." is not entirely true. First, Raman scatter occurs in all directions to a degree, not just in the backward direction. Second, Raman is used to measure much more than just different forms of organic carbon. Rephrase.
- Line 172: More than just "peak temperature and strain conditions" are important for determining the molecular structure of geologic organic carbon. I would argue that biologic origin, depositional conditions, erosion, exposure to oxidants, and microbial activity are just as important as temperature and strain (and perhaps more so!).
- Line 173: The statement "Initially, the carbon will exist in the form of fossilized organic matter." is not correct. Initially all of this organic carbon was from living carbon-based life.
- Line 180: What does "excess inorganic carbon" mean? Excess of what?
- Line 185: Change "lots" to "co-adds".
- Line 188: In figure 3 the caption states that a "Gaussian-Lorentzian hybrid" was used to fit the spectra. This is commonly termed a Voigt or pseudo-Voigt profile. Regardless, which profile shape was used to fit the data.
- Line 204: The statement "The intensity of a single peak is a direct product of signal strength,..." is tautological. Raman intensity is proportional to the fluence of the input excitation source, the number density of oscillators in the probe volume, and the Raman cross-section (itself a function of the molecular polarizability).
- Line 206: The statement "The G-peak is in fact a composite of three spectral bands..." is not correct. For less ordered carbonaceous materials the G-peak is best represented by a single peak, for higher metamorphic grade organic matter there can be another peak or two in there, but for graphene (arguably the most ordered carbonaceous

material) there is only one G peak whereas for single-walled carbon nanotubes the G-peak is split into G- and G+ peaks. What I am saying is that Raman spectra of carbonaceous materials is incredibly complicated and so definitive statements such as this are inappropriate.

- Lines 216-217: What do you mean by "pure graphite"?
- Line 219: The statement "...shows an increase in RBS with increasing temperature at higher maturities..." is tautological. Increased temperature = higher maturity.
- Line 245: The wrong paper by Barker and Pawlewicz is cited. You are looking for Barker and Pawlewicz, 1986, The correlation of vitrinite reflectance with maximum temperature in humic organic matter, Lecture notes in Earth Science, Vol. 5, Paleogeothermics, Edited by G. Buntebarth and L. Stegena, Springer-Verlag, Berlin.
- Line 283: Quantify "weak trend".
- Lines 309-310: Remove "(although reversed)".
- Line 373: The statement "...is kerogen-like carbon rather than coal,..." is misleading. Kerogen is operationally defined as insoluble sedimentary organic matter. Hence, coal is kerogen. Usually, coal kerogen is termed Type I, or gas-prone kerogen. Change statement accordingly.
- Line 404: "... (as noted previously by Muirhead et al., in review)..." I don't love citing unpublished work. Also, this is definitely not "noted previously" as it is unpublished. Finally, this citation is not included in the bibliography. I suggest removing this citation.
- Line 427: The statement "Since the Lahfid et al...." is unclear. Rephrase.
- Line 536: Space needed between "Michael" and "Raman".