

Dear Dr. Nakamura,

Thank you for taking the time to review our manuscript and construct such useful comments. We have found your points very helpful in structuring a revised manuscript, which now focusses on highlighting the specific changes in Raman spectral parameters in detailed transects across the strained localities and comparing these to the burial trends, rather than attempting to compare various geothermometric equations. We believe that this makes the point of the manuscript clearer, whilst also allowing for a future follow-on paper to deal with the geothermometers individually and therefore expanding the scope to include methodological detail appropriate for each equation, as well as independent measures of temperature. We believe that this approach has greatly benefitted the manuscript as we can now focus on the original aim of the study, which was to assess the ways in which strain affects Raman parameters.

As outlined in our responses to other reviewers, our major changes are as follows:

- We have focussed the paper on the changes to individual Raman spectral parameters rather than geothermometric equations, only including the geothermometry as a minor discussion point later on in the text. We believe that this makes the manuscript far clearer and more focussed, not to mention easier for the reader to surmise the key points of the study.
- Transects across faults and shear zones are presented in more detail.
- Error ranges have been added to both text and figures.
- Methodology and definitions have been significantly tightened.

Please see below each of the major and minor comments for specific responses and changes made. We thank you again for your time and effort in helping us to refine the manuscript. Our comments are highlighted in blue text.

Yours sincerely,

L. Kedar, C. E. Bond, and D. Muirhead.

Major comments

1. Before you start to discuss the effect of strain in natural deformed rock samples, you should state a more detailed discussion on the peak metamorphic conditions of “background” samples under low-grade metamorphism. In your manuscript, there are no comments on the peak temperature conditions for “background” samples based on different thermal indicators (such as vitrinite reflectance, mineral assemblages of mafic rock, and illite/chlorite crystallinity) and previous literature. Hence, I am not sure which thermometry is more suitable for peak temperature estimation. Although carbonization depends sensitively on other effects such as tectonic deformation, fluid activity, lithostatic pressure, and duration of heating, there is no doubt that peak temperature is the most important factor during carbonization/graphitization. Therefore, you should compare between estimated temperatures by each thermometry and individual thermal indicators such as IC or mineral assemblages before discussing the effect of strain. In particular, the difference in peak temperature conditions inferred from three different thermometry is very interesting. Each thermometry was empirically calibrated by other

temperature estimations at different localities. This difference might be the key to understanding the effect of other factors including the tectonic deformation during carbonization.

Thank you for this thoughtful comment. We accept that in an ideal world, there would have been at least one method used to independently estimate peak temperature. However, as a result of time, funding, and travel restrictions, we were unable to carry out any of the additional methods listed above. This is part of our reasoning for omitting the geothermometer comparison from the revised manuscript, as we believe that putting it into a dedicated paper in future which deals with these independent temperature measurements would do it greater justice. We do, however, refer to estimated peak temperatures calculated using burial depths obtained from previous literature (Lines 379-382)

2. Three thermometers you applied are optimized for “dispersed” organic material in pelitic rocks, not marl or carbonate rocks. In general, the chemical structure of organic material (i.e., type II kerogen) in carbonate rocks is largely different from that of organic material (i.e., type III kerogen) derived from terrigenous sediments such as pelitic or psammitic rocks. Therefore, you should discuss the effect of precursor material between carbonate rocks and pelitic rocks before discussing the effect of strain.

Please see the previous comment: such precise detail could be easily discussed in a future dedicated paper dealing with the geothermometers as a focus to the study. Our main aim of the revised manuscript is to focus on the ways in which individual Raman spectral parameters deviate from any observed burial trend in locally strained samples, and how these changes are distributed throughout fine-scale transects across zones of high strain.

3. If the estimated temperatures reflected true burial temperatures, the peak temperatures inferred from Lahfid thermometry are inappropriate because it was calibrated in the range between ~200 and 320 degrees C (see a calibration line in figure 4 by Lahfid et al. 2010). Most estimated temperatures (~100-200 degrees C) you demonstrated in Figure 7 are out of calibration range. In addition, I am not sure why you did not apply for Rahl’s thermometry in your study area. Please describe the reason why you select three thermometry.

The original reason for comparing the various geothermometers was to see how they were affected in zones of high strain, rather than being too concerned with the exact temperature values produced by the equations over the complete sequence. However, we appreciate that this could introduce more uncertainty into the results. We therefore think that our revised manuscript – in which we focus mainly on changes in the individual parameters rather than comparing geothermometers – is a more meaningful way to present our results.

4. In L213-215: It should be borne in mind that the significant decrease in ID/IG ratio by Nakamura et al. (2015) and Kirilova et al. (2018) was observed under brittle deformation of “fully ordered” graphite, not amorphous carbon and coal. Other literature mainly treated amorphous carbon or coal as a starting material to assess the change in ID/IG ratio during deformation. The crystallinity of starting material is completely different. Therefore, I think it is problematic to compare between the spectral evolution of graphite by deformation and that of coal and organic material.

It was never our intention to directly compare these different starting materials to one another as we realise that they are indeed completely different, so we are grateful that you have pointed out the fact that this is how it comes across. We have endeavoured to clarify that these situations are incomparable in the figure caption for Figure 4, where we believe the confusion has arisen. This is why Part (a) of Figure 4 has two trend lines: one for amorphous carbon and one for a more crystalline starting material.

5. Raman measurement using a powder sample is a good method to avoid polishing damage during making thin sections. However, it is difficult to recognize the laser damage on the OM surface. According to Nakamura et al. (2019), irradiation-induced depressions of 1.02-3.71 μm are observed at powers of $> 0.7\text{mW}$. Your measurement settings ($<3\text{mW}$) during micro-Raman spectroscopy are slightly higher than the threshold of laser irradiation we found ($\sim 1\text{mW}$). In general, the registrability of laser irradiation is dependent on the crystallinity of OM and laser wavelength. Your samples are much weaker than the natural OM we analyzed. Hence, it is necessary for more careful analysis to avoid laser-induced heating and amorphization during measurements. It should keep in mind that down-shifting of D and G bands occur easily by laser-heating.

Thank you for pointing this out – we made an error in the writing of the methodology and actually used only 10% laser power which equated to 0.3mW at the sample surface. Therefore, burning was not an issue. We have corrected the text to reflect this (Line 241).

6. L35: Before you comment on the fold-thrust systems, it is better to discuss on the “ductile deformation” may enhance recrystallization of natural OM (See Ross and Bustin, 1990 and Bustin et al. 1995).

Thank you for highlighting this; we believe we discuss ductile deformation in sufficient detail in our description of the outcrops (e.g. Lines 206 to 219). See also Kedar et al. (2020).

Sincerely,

Yoshihiro Nakamura

Geological Survey of Japan, AIST

Specific comments

L13: I am not sure which parameter you indicate. Please indicate the four most common Raman spectral parameters and ratios in this sentence.

These have now been added (Lines 11-12): “...the most common Raman spectral parameters (peak width, Raman band separation) and ratios (intensity and area) change...”

L15: Please specify the D, G band, IG/IG, FWHM [d], Raman band Separation, and R2 ratio.

See above comment.

L21: upto => up to

Thank you for pointing out this mistake

L27: Ferrari and Robertson (2001) is inappropriate for reference. This paper discussed on wavelength dependence of Raman spectra of amorphous carbon under excitation from NIR to UV lasers.

Thank you for highlighting this oversight. The reference has been removed from this sentence.

L43: I_D/I_G , $I[D]/I[G]$ or R1 ratio are more commonly used.

Thank you. We have chosen the notation to be consistent with Kedar et al. (2020).

L44: peak area ratio (R2) => peak area ratio [R2 ratio = D1 band / (D1 + D2 + G bands)]

As the R2 ratio is defined in more detail later, we felt that to define it to this extent here would read clumsily.

L84: It is difficult to recognize the "level of strain" in natural rocks. Have you ever found more quantitative strain markers in your rock samples (grain size distribution of recrystallized quartz or strain marker such as Radiolaria)? Your classification "background" and "strained" is hard to understand for readers including referees. Please revise to be clearer.

This was also highlighted by J. Rahl in his comments – we have added a more detailed description as to how background vs. strained samples were defined (lines 99-124). It was harder to quantify the strain levels in the rocks than, for example, in our 2020 paper (Carbon ordering in an aseismic shear zone: implications for Raman geothermometry and strain tracking, Kedar et al., 2020), where the shear zone in question occupied a single lithological unit. In the current manuscript, several faults and shear zones involve multiple lithologies, and therefore most sampling was based on judgement in the field. This strategy is better explained in the additional text mentioned above.

L92-93; If so, it is better to describe the detailed occurrences of dispersed organic materials in background and strained rock samples.

Thank you for this suggestion. A comment has been added to Line 133 which reads, "most organic material was located between calcite grains and within seams of insoluble material."

L161-164: Effect of ductile and brittle deformation in natural rock samples is very important to assess the strain-induced carbonization or amorphization of natural OM. Please state more detailed comments how ductile and brittle deformation took place.

It is beyond the scope of this study to fully analyse how the deformation took place on multiple scales and is only mentioned in Section 3.2 to provide some context when describing the samples analysed.

L186-192: Peak deconvolution and fitting function are strictly defined by each equation. For Kouketsu equation, the peak temperature (= D1 band FWHM) fluctuates drastically depending on whether the D4 band at 1250 cm^{-1} is fixed or not. Hence, it is very important to follow the recommended method.

Thank you for highlighting this. Now that our paper focusses on the individual parameters changing with strain rather than comparing different geothermometers, it is worth bearing this point in mind for any future paper which might focus on the thermometers themselves.

L200: $\text{cm}^{-1} = > \text{cm}^{-1}$

Well noticed!

L209: kerogen-like carbon is not commonly used. Amorphous carbon? In addition, Beyssac et al. never comments on carbonization in this paper. It is better to refer to other papers such as Levine, (1993) and Oberlin, Bonnamy, & Rouxhet, (1999). See Levine, J.R., (1993). Coalification: The Evolution of Coal as Source Rock and Reservoir Rock for Oil and Gas. In Law, B.E., & Rice, D.D., (Eds.), Hydrocarbon from Coal, 38 (pp. 39–77) and Oberlin, A., Bonnamy, S., & Rouxhet, P.G., (1999). Colloidal and supermolecular aspect of carbon. In Thrower P.A., & Radovic L.R., (Eds.), Chemistry and Physics of Carbon, 26 (pp. 1–148). New York: Marcel Dekker, Inc.

Thank you for these suggestions and advice. “Kerogen-like” has been changed to “amorphous” (Line 279), and we have followed up on the correct citations.

L250-253: This is not the equation I know! Please explain why you change the parameter from RA1 to R2 ratio.

The two ratios – although not exactly the same – are similar in that they both deal with peak areas. The intent was to investigate how the thermometer results would change with strain and so exact results were not considered too important. However, the Lahfid equation is now not included (see above comments).

L269-275: Please add one sigma error bar in your figures. Your figures are unkind to readers and referees when I check the variation of Raman data between background and strained rock samples. If possible, please add the table in your manuscript.

Error bars have been added to figures where appropriate.

L329: The change in ID/IG ratio is much complex process. According to comparison between natural Organic material and pyrolysis samples by Nakamura et al. (2019), the I_D/I_G ratio shows both trends in increase and decrease with increasing peak temperatures (Figure 5d). On the other hand, simple pyrolysis experiment suggests that the OM shows a systematic increase in the ID/IG ratio with increasing pyrolysis temperature and heat treatment time (Figure 7d).

We are aware that ID/IG changes are indeed complex and likely to be impacted by multiple factors, as you suggest. There is a lifetime of study in this field! We have added the suggested work as a citation (Line 397).

L358-359: I don't think so. Please refer to Nakamura et al. (2019). The significant change in RBS is widely observed in the temperature range between 180 and 280 degrees C (See Figure 5e). The systematic change in RBS is consistent with the change in illite crystallinity.

Thank you for pointing out this oversight. We have changed the text accordingly (Line 432) and added details from Nakamura et al. (2019) (Lines 438-440).

L365: plane,. => plane.

Changed. Thank you.

L383: Please add the mean value and one sigma error of R2 ratio. I am not sure this drop (6-20%) is important or not.

Errors have been added.

L394-395: The equation by Schito and Corrad (2018) was calibrated in the range of %Ro between 0.3 and 1.0 % (L242-244). I think that applicable range of vitrinite reflectance is much lower temperatures than expected temperatures under sub-greenschist facies. Have you checked the vitrinite reflectance of studied samples before micro-Raman analysis?

This is perhaps correct, although calculated values were within the applicable range of temperatures. The intention of looking at this geothermometric equation is to investigate how the results might potentially be affected by strain in certain samples, and therefore how they deviate from surrounding values, rather than the precise numbers being important. We have changed the emphasis of the paper to focus more on the parameters anyway, and now only include the Schito and Corrado equation as a discussion point. As for vitrinite reflectance, we were unable to carry out this analysis for this particular study owing to travel restrictions and time constraints, but perhaps if the aforementioned follow-on study were conducted, this would form an integral part of it.

L401-402: See an above specific comment in L358-359.

See above response.

L406: +/-10°C => ± 10 °C

Format corrected.