Solid Earth Discussions

Solid Earth Discuss., referee comment RC2
https://doi.org/10.5194/se-2021-70-RC2, 2021

Comment on se-2021-70

Jeffrey Rahl (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-RC2, 2021

General comments

The manuscript by Kedar and others presents an investigation into the influence of strain on estimates of peak metamorphic temperature derived from Raman spectroscopy of carbonaceous material (RSCM) thermometry. This is an interesting topic, well worthy of study. RSCM thermometry is now a popular and widely used tool to address a range of geologic problems. The transformation of organic material is generally interpreted to reflect increasing temperature; the authors here explore the extent to which strain may also influence the structure of organic material. If such effects are significant, they would need to be studied and accounted for in future RSCM thermometry studies.

Despite the relevance and interesting nature of this problem, I feel the study could be improved in several key respects. First, for a project striving to document the relationship between estimated temperature and strain, I found it disappointing that no attempt was made to quantify strain. The samples are grouped into two categories ("strained" or "background"). The abstract describes this latter group of samples as "unstrained" (lines 19 and 21), though the body of the paper makes clear that the "background" samples may also be internally deformed, just less intensely than rocks associated with thrust faults or shear zones. Strain, of course, is not a "yes/no" property, but rather one that varies continuously in nature. It feels like a lost opportunity to not investigate the relationship between the magnitude of strain with the observed Raman spectra. The authors did collect samples along transects perpendicular to the faults/shear zones studied which could perhaps be used in this way if a strain gradient is present (this is unclear from the location descriptions). But as far as I can tell such an analysis was not presented in detail. (The key to Figure 5 states that samples structurally above or below the faults were at a distance of 5 m, though that does not fit with the text in section 3.) I think more specific characterization/analysis of the strain/structural position of the studied samples would be a valuable addition to this study. For example, I would be intrigued to see a figure showing the various Raman spectra for individual sample transects, illustrating how spectra evolve with distance to the fault (especially if an assessment could be made of how strain magnitude varies with position).

I also have questions about the acquisition and analysis of the Raman data. The authors report fitting for two peaks in the Raman spectra, a "D" peak and a "G" peak. While I am

not an expert on carbonaceous matter, I understand this to be a significant oversimplification – and importantly, a departure from the previous studies relied on here. Observed Raman spectra of organic material over these wavelengths are generally understood to be composed of a series of bands that correspond to different types of defects/impurities (the Henry et al., 2019 paper cited by the authors has nice discussion of this). The thermometers that the authors utilize in this study (e.g., those by Lahfid et al., 2010 and Kouketsu et al., 2014) do not rely on the simplified composite "D" and "G" peaks used here but rather on the underlying bands (D1, D2, D3, D4, and G). Thus, I do not understand how the authors can claim to be using these thermometers when they have not estimated the required input parameters.

My last significant comments are about the presentation of the data and the lack of consideration of errors/uncertainties. The presented plots show points without any sort of error bar, despite the fact that uncertainty resides in both the estimation of each measured parameter as well as in the underlying thermometry calibrations. Errors are mentioned in a few places in the text, but these are not presented anywhere, including in the supplemental data table. I feel these issues are significant and should be addressed in a revision. I would also appreciate clarification on the dataset; the Supplemental data table contains results for 26 samples… but I count about 35-ish samples in Figure 5, and Line 180 references 62 samples. I understand that some of these have been averaged together somehow (though it is unclear to me how this was done – was sample material mixed together, or were data from various analyses averaged together?) It would be best to include all samples in the data table, along with uncertainties as well as sample locations (UTM or lat/long). My impression is that, in practice, errors in RSCM temperature estimates may be at least 30 degrees C and likely larger. Something like this is implied by the variability in the presented temperature estimates (Figure 7). An important issue for this study – and not one really explored in detail – is how the magnitude of changes in strain-related temperature estimates compares with this uncertainty inherent in RSCM thermometry. Is this influence small relative to other sources of uncertainty (in which case it could be perhaps be ignored) or is it a major effect?

This is an interesting problem and the authors have done a lot of good work here. I wish them the best as they revise this manuscript!

Jeffrey Rahl

Washington and Lee University

Lexington, VA, USA

August 29, 2021

Specific comments

Line 89 – "background" strain? Given the purpose of this study, assessing and describing this "background" strain is important. Can the strain in these rocks be quantified?

Line 95 – one sample or a cluster? I don't understand what was done in practice here. How closely spaced were samples in a "cluster"? How were they averaged together? (Physically, or were analytical results averaged?)

Line 190 – I am confused on the analytical procedure used here. Above (line 185) it says that for each sample, 10 grains were studied, and that each grain was scanned three times. That would make 30 analyses per sample. Yet here it says "this process was carried

out 3 times for each acquired spectrum, resulting in 30 analyses per sample" – This seems to be referring to the data processing steps, though I don't understand why performing these steps multiple times wouldn't produce the same results for each spectrum. And further, I don't understand where the 30 analyses stated here comes from (10 grains * 3 acquisitions per grain * 3 "processes carried out for each spectra" = 90, not 30).

Line 245 – how is Ro_eq determined from the Raman parameters? (i.e., what equation is used?) It is strange to provide these equations here but still require the reader to go back to Schito and Corrado to see how the Raman parameters come into play. I think there is no reason to include the equation for T1 here without also presenting the method to determine Ro_eq.

Line 281 - "high error causes these ranges overlap" What are the errors? How are these determined? They are not shown on the figure nor in the supplemental data table. Why not plot the error bars associated with each sample on the plots?

Line 295 – "… or that the equation is not applicable in this instance due to the Raman parameters used"? What is meant by "due to the Raman parameters used"?

Line 400 – this is difficult for the reader to evaluate because the equation incorporating this parameter is not provided

Line 420 – "significant variation on a sub-km scale" – what, specifically, is meant here? (put a number of the variation; this is relevant for the following discussion)

Section 7.8 – The RSCM thermometers investigated in this study are assessed here, based on how much the estimated temperatures differ for the "strained" and "background" samples. For instance, the Kouketsu thermometer is stated to be "more suited to strained environments" because the strained and background samples give similar results (line 431). But I think this misses the point. The goal of this entire process is to, as accurately as possible, estimate the peak temperatures experienced by rocks. A given thermometer equation can yield results that are insensitive to a particular factor (such as strain), but that does not mean that it produces reliable estimates. A key question is, does strain organize organic material in a fashion similar to increasing temperature? If so, I think the goal should be to build a model that connects the nature of the CM (as measured via Raman) to both temperature and strain. It would be ideal if the study had been conducted in a setting where independent estimates of temperature were available (like in the various studies used to calibrate versions of the thermometer). Without this, the authors need to rely on the internal consistency of the results, which can provide interesting insights but can't address the question of which of the applied thermometers gives the most reliable results in the study area.

Line 432 – "lower than expected for the region…" – on what is this expectation based? In the earlier part of the paper, all that is said about these rocks is that they are "subgreenschist facies" – there don't seem to be any detailed controls on peak temperature here.

Line 433: "shows variation in temperature predictions on a sub-km scale, making it less suitable for general use" – I'm not sure what is meant by "general use" here, and I also don't follow the logic. I interpret this to mean that the temperature estimates made using this thermometer are noisy, and therefore unreliable. I worry the authors underestimate the uncertainty inherent in these techniques.

Line 435: "… demonstrates a more consistent error…" – what is a "more consistent error"? There are no independent estimates of the temperature for these rocks, so there doesn't seem to be a way to estimate the accuracy of the various thermometers. Do the authors

mean that the results for the Lahfid equation for the strained samples are consistently biased in the same direction? I think that is different than having a "consistent error", which I would take to reflect the magnitude of a temperature difference from a true value.

Line 435: "…the predicted temperatures are more in line with those predicted for the area…" Again, based on what? There don't seem to be any independent temperature estimates.

Line 460: "… an equation is required that can resolve temperature changes over hundreds of metres at the least" – is this even feasible? There are errors in all of these measurements.

Line 461: "we conclude… choosing the most appropriate equation is complex and dependent on multiple factors" – what are the "multiple factors"? The preceding discussion suggests that strain is one, but I'm not sure what else is meant here.

Line 465: "The use of multiple parameters… suggests that the equation should be relatively insensitive to strain" – I don't understand this. If any of the parameters that go into the temperature estimate are influenced by strain, why wouldn't that influence the results? Why would including other parameters limit the influence of parameters sensitive to strain?

Line 468: "The use of multiple terms in the equation may help to produce more reliable results (as the influence of different parameters interact)" – why? The logic here is not clear to me. I think what matters is the inclusion and appropriate weighting of the relevant parameters, not the number of terms in the equation.

Technical corrections

Line 21 – should be "up to 140"

Line 100 – grammar (replace semi-colon with " and…")

Line 171 – Reword; the text here implies that Raman spectroscopy works only on organic carbon.

Line 178 – Is "pertaining" the right word here?

Line 261 – should be "detail", not "detailed"

Line 277 – units should be included with these values

Figure 4 – why are some of the grey lines dashed rather than solid? There is no explanation for this on the figure or in the caption. Other than this and the lack on uncertainties shown on the data, the figures are very attractive and quite helpful, especially the maps and cross sections (good work!).