Solid Earth Discussions

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Comment on se-2021-70

Yoshihiro Nakamura (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-RC3, 2021

Dear Dr. Lauren Kedar,

This manuscript represents a detailed investigation of organic material (OM) combined with field observations and spectroscopic analysis in deformed rock samples. It is widely known that recrystallization and degradation of dispersed OM (so-called carbonization) in sedimentary rocks is closely related to tectonic deformation, catalytic effects, and fluid activity under lithostatic pressure. I think that presented data by Kader et al provide important information on the effect of strain in the fault-thrust system under low-grade metamorphism. Such data must help to understand strain-induced carbonization/graphitization from amorphous carbon to turbostratic, and then graphitic carbon under complex natural conditions. However, I have a few major concerns regarding your present manuscript. More detailed major and specific comments are listed as follows. I hope my comments help to revise your manuscript.

Major comments

- 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.

- 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.
- 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.
- 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.
- 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 > 0.7mW. Your measurement settings (<3mW) during micro-Raman spectroscopy are slightly higher than the threshold of laser irradiation we found (~1mW). 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.

Sincerely,

Yoshihiro Nakamura

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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.

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

L21: upto => up to

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.

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).

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

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

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.

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

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.

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.

L200: cm^{-1} = > cm^{-1}

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.

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

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.

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).

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.

L365: plane,. => plane.

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.

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?

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

L406: +/-10°C => ± 10 °C