Comments on se-2017-74-manuscript-version3
"Structural disorder of graphite and implications for graphite thermometry"

The revised version of the manuscript corrects some of the issues, which had been raised by previous reviews by R. Kilian and Oohashi Kiyokazu. However, the main points that had been criticised (interpretation of R2, sample deformation, R2 relation with deformation) and which are essential for the key message of the contribution remain not satisfactorily addressed at all. The authors add additional data or data treatment which, as outlined below does not necessarily help the authors to strengthen their argument against the criticism raised by the reviewers.

In short, the main issues were and still remain to be: 1) increase in R2 needs not to be equivalent to a decreased graphite structural order. 2) The "correction" for shear strain is actually not a correction and the relation of bulk sample strain to deformation which is actually resolved in the slip zones (see below) remains unclear. There are minor issues related to (a) the speculation on deformation mechanisms , (b) the way strain is treated and (c) how the total frictional work was calculated.

The message of the study seems to be that the graphite Raman thermometer is not applicable as-is in deformed rocks. However, the additional interpretations that go into the manuscript (e.g. effect of pressure and sliding velocity, deformation mechanism of graphite in these experiments) are not very well backed by the data and only deflect from the key message.

I recommend that the main issues need to be addressed to make this manuscript a robust publication. The experimental data (at best the raw data, displacement shear-stress, and including sample thickness data) and the Raman data are valuable to provide an insight into the great weaknesses of this Raman thermometry method and to start to understand the influence of deformation on the R2 ratio. However, the partly insufficient data treatment and presentation (e.g. experimental data, bulk strain estimates and sample thinning vs deformation in slip zones, or for example claims on grain sizes and microstructures in the text which are not in accordance with what the figures show) or the speculative interpretation (claims on deformation mechanism and R2 origin) is not what this kind of data has deserved. I am sure the authors could do better, also in cutting short in the speculations and strengthening the analytical parts by more coherent interpretations and a better description of methods for example.

1) Origin of reduced R2: The authors claim in numerous passages of the manuscript to report a reduced crystallinity (and it seems they define crystallinity by the presence of intragranular defects, or crystallographic perfection) of graphite. However, what they actually show is a ratio of peaks obtained from Raman spectroscopy (R2). The increase of R2 may be associated with increased intragranular defects or a reduced grain size (as already mentioned in the two previous reviews). It is further claimed that grain size reduction cannot account for the observed change in R2 - a claim the authors do not provide any evidence for. An increase of intergranular lattice defects is pure speculation and actually, newly provided data in the form of TEM images shows the opposite and are not in accordance to what the authors write in the manuscript. While stating that Raman measurements are obtained from within grains (which are said to be >10 µm - where does this number come from, Figure 4b? I'd strongly disagree that any grain size is evident from this Figure and if so, that 10 µm may be the lower limit), TEM images of the slip surface from where the Raman spectra were obtained show nanometer scale grains. By providing the TEM data, the authors actually contradict what they write in the text, as the data nicely shows that grain boundaries are produced and grain size is largely reduced with grains at the scale of several 10s of nm.

It is nicely demonstrated is that within slip surfaces, R2 is increased and the grain size is very small. What is not shown anywhere is that the increased R2 is related to an increase of intragranular defects - but exactly this is stated throughout the manuscript.

To overcome these ambiguities, providing a definition of crystallinity might be helpful. A crystal may have a low crystallinity because of a high density of (intragranular) lattice defects, however alternatively, an aggregate of "perfect" but extremely small grains may have a low crystallinity since there is a considerable volume which may be influenced by the disorder induced by grain boundaries. The latter definition would go very well with the presented data. Still, with the available data, nothing can be said about the intragranular defect density.

2) To correct the graphite thermometer for strain or not:
The authors present a fitted function (with surprisingly many digits) for R2 as a function of bulk shear strain or total frictional work. While they correctly note that any sort of strain-related correction will most likely never be feasible in nature (since it is most likely impossible to determine the amount of deformation within a specific graphite aggregate) I do not understand how this fitted function will be a "correction" for the thermometer. Shouldn't a correction provide the "true" R2 after removing the effect of deformation? That's not what the presented functionality provides.

3) The authors report that most of the strain is accommodated in thin slip surfaces. The variation of apparent bulk shear strain is due to sample thinning (unclear whether extrusion or compaction) so I would not expect this to principally affect the shear surface thickness since they seem to be consist of already highly compacted material. Hence it is pretty surprising to see a relation with the apparent bulk shear strain and R2. Using the mode of R2 instead of the mean, this relation actually becomes not so clear anymore. What is actually the reason to use the mean R2 and not the mode (e.g. by assuming that the most likely result will be analysed) of R2? Even when one would want to assume a relation between bulk strain and strain in slip zones, the chosen measure for strain is at most one of apparent shear strain, and it is not a 1:1 relation with the deformation within the sample. providing shear stress - displacement and displacement - thickness curves may already help with the interpretation of the data.

4) Calculation of total frictional work:
The authors included as an alternative measure to strain the total frictional work, given by the shear stress integrated over the displacement. I cannot reproduce the results presented in Figure 3 or Table 2 using the data of the authors shown in Figure 1a. Also, just by visual inspection, I do not see where the large differences between e.g. experiment8, 9 and 10 may arise from.
Unfortunately for experiments 2, 3, 6,7 no displacement - friction coefficient data was provided. I recommend to double check the calculation procedure for the frictional work and to supply for all experiments displacemnt-shear stress curves. Additionally, it would be beneficial to provide also to provide the displacement-thickness relationships, such that the data could be adequately interpreted.

Following some additional comments with reference to the text:

L57: maximum grain size of 160µm : the maximum is in general a very unfortunate measure to say something about a material.
L74/75: .".. and summing." summing over?

I'd also still argue that the measure calculated by the authors is not a shear strain by it's definition in the sense that no strain ellipsoid could be derived from it and it is at best an apparent shear strain. The larger the thinning of the sample, the less related this number is to the deformation of the material. To describe the amount bulk deformation within the material e.g. the aspect ratio of the strain ellipsoid would be more meaningful. However, also for any of these consideration, it needs to be understood whether the sample is loosing volume (is compacting) or extruded somewhere.

Same for Section 3.1.2: While it is stated that the shear strain increase towards higher displacement velocities is basically an artefact of sample thinning (unclear whether extrusion or compaction), this fact is largely neglected in the rest of the ms. However, it not clearly noted that the choosen measure of deformation is with increasing sample thinning increasingly unrelated to the amount of deformation within the sample.

L84: Note that the laser spot size is not 1:1 equal with the Raman spot.

L141/142: "The degree of crystallinity in each sample..." Statement only makes sense when crystallinity would be defined as per aggregate - adding the option that grain boundary density increase decreases the overall crystallinity.

L147: "..crystallinity varies within each sample see above and speculation, first of all it is R2 which is variable.

L151/52: "Furthermore,...." a) table shows R2 not crystallinity as apparently defined by the authors. b) R2 actually increases (!) with increasing sliding velocities.

L156: work not "force" - also please check calculation procedure.

L166/167resp. Fig. 4b: grains of 10-50 µm size: unclear if grains or aggregates? Even if these are grains, it does not look like 10 µm is the lower limit. Also compare with the TEM images or Fig. 4d,e
Overall, entire section 3.3.1 does not convincingly demonstrate the large, 10 µm grains within the slip zones.

Section 3.3.2: Figure 5.a if grains are just a few 50-150 nm thick, how would measurements not be covering also grain boundaries. Kinking in graphite (if it is not twinning, but most angles seem larger than the typical twinning relation), Fig. 5b,c requires interlayer slip - and in case this is not crystallographically controlled will result in (001) parallel boundaries, and (001) perpendicular boundaries at kink boundaries, so this is another nice evidence for an increased boundary density beyond the Raman measurement scale. Fig. 5d: I'm not sure what I am seeing but are the authors sure this isn't already beam damaged material?

L200ff: "...shear strain variation systematically related to the condition of the experiments...shear strain is directly dependent on the applied normal stress". again, the value the authors calculate as shear strain is not a 1:1 measure for the amount of deformation within the material and an artefact of sample thinning.

Section 4.2 Structural disorder of graphite
largely this section should talk about R2 and what was really seen,. e.g. in the TEM images. it is NOT demonstrated that highly crystalline graphite is transformed into disordered graphite with strain!

What can actually be said is that large annealed grains show a low R2 and the deformed material has a (nano)scale grain size, increase of boundaries (grain boundaries, tilt/kink boundaries, ...) and a high R2. It's not possible to say something about crystallinity at the grain scale in the sense of intracrystalline defects.

L223: "...the results overall validate that structural disorder of graphite can result from shear deformation..." It is close to extremely enigmatic to me how this could be more than a speculation and how the obvious grain boundary area increase is totally ignored.

L229:230: How is it possible to say that no grain boundaries were measured if a) it is not clear where exactly the measurements were undertaken (see question and request from my first review) and b) TEM images of the slip surface show grain boundary spacing at the nm scale and c) the 10 μm grain size remains a speculation (it's totally unclear to me where this number comes from)? Is that some measurement or eyeballing?

L233:30: "...to disorder of the internal structure of graphite rather than grain size reduction." Please see above. This is not consistent with the images you provide!

L241: "...proven..." a) not a proof , b) not shear strain

L249: "We demonstrate that during shearing higher normal stress results in increased shear strain" No. And if layers thin just by compaction (volume reduction) I'd call the latter the reason, not a higher normal stress.

L257:"...effects of shear strain and pressure..." a) if anything at all, the only measure investigated was a bulk apparent shear strain and not pressure but normal stress. Depending on confinement, the pressures my vary of course, but I don't see how to derive/separate a pressure effect from that. Especially since the deformation of graphite seems to happen in very thin slip zones.

L269ff: "...fractured grains...", "brittle processes operated during shearing..resulted in structural disorder of graphite". While fracturing is for example and certainly intimately related to dislocations, it inevitably creates grain boundaries! A more thorough discussion on graphite deformation mechanism might also be more helpful.

L273: "...would not induce temperatures high enough fro crystal plastic processes" What are those for graphite? And processes such as?

L276: The authors probably mean crystal plastic mechanisms.

L277: Plastic deformation? It should be ductile deformation.

L281: "The crystallographic structure measured by Raman..." No, D1,D2 peaks are measured which could be interpreted in certain ways, e.g. related to structural state of a crystal lattice or e.g. grain boundary density, density of impurities... .

L285: "...mechanical modification of the graphite structure, which this study has identified..." No, the authors have identified an effect on R2, not directly on the graphite structure.

L286: " in deformed rocks" misleading, no rocks here beyond a pure graphite gouge.

L299: "...we propose a appropriate adjustment based on our dataset" I don't find - beyond my and the authors doubts on a useful applicability of such an adjustment - any suggestion how this adjustment should look like.

L307: "Furthermore, it can be challenging to estimate shear strain in nature ..." Yes it can be challenging and it will be even more challenging to translate bulk rock strain to a deformation seen by a particular grain of graphite within a deformed rock.
It should actually also be noted that in the experiments it does seem challenging to estimate the true shear strain/deformation in the bulk: and even more challenging to estimate the deformation in the actually deforming layer of graphite and this is what would be required to start any correction at all.

L310: "... graphite crystallinity.." use R2 instead of crystallinity unless properly defined

L312: ""...graphite structural order" see above, use R2

L313: "Microstructural data reveal that this is a result of brittle processes." This needs to be clearly laid out in the results and in the discussion.

L314: " trend of increasing shear strain as a function of normal stress and sliding velocity..." this is an effect of sample thinning. And not that this shear strain is does not 1:1 relate to deformation seen by the bulk sample.

L318: "...simple shear strain calibration.." a) there is no such thing as "simple shear strain", this is nonsense b) there seems to be substantial thinning of the samples, and while incorrectly treating it as simple shear to calculate an apparent shear strain, the data does not relate to simple shear flow.

Rüdiger Kilian