Interactive comment on "Structural Disorder of Graphite and Implications for Graphite Thermometry" *by* Martina Kirilova et al.

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In the manuscript "Structural Disorder of Graphite and Implications for Graphite Thermometry" s2-2017-74, Kirilova et al. report the results of Raman spectroscopy on an experimentally sheared, synthetic graphite gouge. Raman spectroscopy on carbonaceous material (RSCM) has become a frequently used geothermometer assuming that the crystallinity of graphite represents peak metamorphic conditions. In contrast to geothermometers based on mineral compositions where a retrograde overprint can often be easily recognized, preservation of peak metamorphic conditions under deformation might not be easily recognised in graphite where no compositon changes are to be expected. Accordingly, this contribution is of special interest to researchers, either using RSCM or having to evaluate RSCM derived data. Testing the RSCM thermome-

ter against experimentally deformed graphite gouge is novel and the results of the presented study are very interesting and strongly suggest that the applicability RSCM thermometry to deformed rocks - and accordingly to almost all metamorphic rocks - needs a careful evaluation. This ms highlights that not all parameters to unequivocally interpret RSCM are sufficiently understood. The authors of the ms suggest a correction of the RSCM thermometer based on shear strain, related to their observations in the synthetic graphite gouge.

The manuscript is concise, easy to read and provides a valuable insight into a neglected problem of RSCM. However, there are points that are either not entirely consistent, that need further clarification or corrections, especially in the obtained relation to sample strain and the determination of crystallinity and those should be addressed (listed below). Overall I recommend that the manuscript is suitable for publication after moderate revisions.

Following comments should be addressed.

1) Relation to strain/stress a) A "shear strain" is calculated by summing up the ratios of displacement increments and thickness. As it appear the samples are thinning with increasing displacement, this "shear strain" is neglecting the thinning component, the derived "shear strain" can not be used to calculate a strain ellipse (no functional relation) and overestimates strain in the sample. A more correct procedure would be one where progressive simple and pure shear are treated to occur concurrently, and reporting a unique measure of strain. b) The authors report (and obtain their measurements) from the shiny surface where they assume along which most of the displacement is realised. Assuming that this surface is actually a thin layer, the strain within that layer must always be larger than the strain derived from the entire sample. Hence one might speculate that a functional relation between the determined "shear strain" and R2 is at best a rough approximation. In case, as indicated by some of the comments on the microstructure, the compaction (sample thinning?) is localised as well and not homogeneous, a bulk sample, "strain estimate" is even more likely to be unrelated to the

state of deformation in the analysed layer. c) The authors use a mixture of surface related measures (friction coefficients, normal stress, slip rate) and volume measures (strain) which might be confusing in places, e.g. it might not be directly evident that the experiments with the 25 MPa normal stress should actually be stronger that the 5 MPa experiments.

2) R2 correlation with shear strain a) Following the number in formula 1and as shown in Figure 3., shear shear is evaluated as a function of R2, the inverse would be logical and a fit is numerically not equivalent. Additionally, formula 1 is wrong. b) What is the physical basis that R2 and strain should have a power law relationship?

3) Origin of D1,2 bands Obtaining Raman spectra at surface ledges on (001) or generally grain boundary regions, the appearance of the D bands has been observed (e.g.Tuinstra & Koenig, 1970; Pimenta et al. 2007). For small grain sizes, the ratio of G and D bands is actually used to establish a grain size determination. The authors mention that the increasing area of D1,D2 peaks is related to a decreasing crystallinity of graphite, is it possible that the crystallinity does not change but rather with a smaller grain size more grain boundary area with a disturbed lattice is measured? The authors estimate the minimum resolution of their optical system at 0.4 μm, however, from the text it becomes not clear whether this relates to the analysed point and/or if the analysed point could actually be identified and if so, whether measurements with a large R2 come from areas with a smaller grain size? If crystallinity is defined in relation to intragranular defect density/lattice perfection, it should be verified that only intragranular measurements are evaluated. If the grainsize is so small that most likely grain aggregates are measured, maybe the grain size effect could be corrected. The authors mention that they actually examine the structural disordering of graphite, so depending how this is defined, it needs to be considered separately to grain boundary effects.

4) Applicability of a strain corrected RSCM thermometer a) in real rocks, it might be difficult to estimate strain and it might not be clear in which way deformation partitions between graphite and other minerals and so I'd encourage the authors to share

some thoughts on how a strain correction should be applicable in a real-rock situation.ÂăÂăÂă b) A correction for the thermometer might depend on the relation of temperature and strain: e.g. during exhumation of a rock deformation takes place at increasingly lower temperature. Using a simple "strain" correction, would imply that the deformation temperatures during exhumation would not have to be considered. Given that most minerals show different deformation mechanisms at different temperatures, it might be reasonable to assume that this is the case as well for graphite. So strictly speaking, a correction should only consider lattice defects introduced by the identical process which is occurring in the calibration experiments. I'd encourage the authors to comment on this complication of such an effort. c) Using any thermometer to determine peak temperatures, often the measurements yielding the highest results are considered as representing peak conditions to overcome the problem of a partial lower temperature overprint. Given that some measurements in deformed samples still yield a low R2, it would be helpful to see where those measurements are actually determined. Are those from within grains while those with large D and D' bands contain areas with a high grain boundary density?

The manuscript and the reader would benefit from some definitions: crystallinity (vs structural ordering for example), interpretation of the peaks/bands in the Raman spectrum, (G being sp2 activation, D1 most likely to intraplane defects and D2 to out-of plane defects, sp3 defects ...) should be introduced and defined. Why are sliding velocity, slip rate, shear velocity are all used synonymously? The figures regarding the microstructural description might benefit from a better resolution since some feature referred to in the text cannot be seen in the figures (comments below).

Minor comments on the manuscript (l=line): l 41:friction coefficient l 52: no "or" l 54: 160 μm are maximum grain size? l 54: annealed instead of "cooked"? l 85: Please introduce G,D1,D2 l 102: coefficient (please also correct that in the figures if you prefer to stay with friction coefficients instead of shear stress) l 103: coefficient l107: Plots of μ at all slip rates ..: I do not see the gradual decrease of μpeak (numbers, if I'm not

mistaken are 0.43, 0.43, 0.41, so I wouldn't call this a gradual decrease) l 108 slip rates ...shear velocity: is there any difference? Elsewhere like in the tables there is slip rate, sliding velocity, why are they all used synonymously, please settle for one term. l 110: Where are values of μss are read off? l 135: retained instead of produced l 137: varies l 140: high-pressure experiments: should be high normal stress experiments l 152: fractures with random orientation compared to the slip direction: I can't see those l 155: ...well-compacted layer Fig 4c: hard to see in the Figure what is described in the text l 156: "randomly oriented ... Fig 4d": Is that actually confirmed or just based on visual impression l 158: "weak fabric development (Fig. 4e)" I can't see this in the figure l 159: "filled with smaller graphite grains...Fig 4f": also here, it is hard to see, I hope a better resolution of the image and some arrows may help l 176: "more efficient reorientation" What should that be, rotation per time, alignment after strain...? l 178: This clear trend is not so clear to me. l 180: "partial frictional heating": What should that be? l 183 ff: The relation of compaction (volume change), thinning and the apparent dependency of "shear strain" on normal stress and displacement rate should be reconsidered, given that no suitable measure for strain is used l 188: replace high-pressure with high normal stress l 207: "stable mineral" from the thermodynamic point of view it is the stable mineral, so please explain your definition of "stable". l 291-223: There is a mixture of lithostatic pressure and normal stress: Any effect that is observed at higher normal stress does not mean there is a "significant effect of lithostatic pressure". Normal stress is not equivalent to confining/lithostatic pressure. l 234: "... microstructural observations provide some indications of the deformation processes..." These observations could be enhanced! l 239: "plastic mechanisms" Such as? l 240: "plastic deformation" What should that be in contrast to the presented experiments where a gouge seems to flow by a rate independent mechanism? l 244: "crystallographic structure ..." This seems to be a speculation neglecting a grain size effect. l 262ff: Any fit should consider the measure of strain as the independent variable, not as shown and calculated as the dependent one. Independent from that, (1) is not correct. l 273: "We observe a trend..." So it appear there is an increasing thinning which however needs not to translate into

an increased shear strain. l350: "approximate average crystallinity": What should that be?

Figures and Tables:

Table 1 and table 2 are mostly redundant and differ just by 1 column. Figure 1 It would be nice to use identical colors in (c) and (d) representing the displacement. Y-axis should read friction coefficient. Figure 4 could strongly benefit from some images that more clearly show what is described in the text.

Supplementary material: If "int" stands for intensity and "pos" for wavenumber, it seems like the column headers are misplaced.