

Interactive comment on “Technical Note: Aeolian dust proxies produce visible luminescence upon intense laser-illumination that results from incandescence of internally mixed carbon” by L. Ma et al.

Anonymous Referee #2

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The authors present an interesting approach to assess the presence of black carbon (BC) comingled at low concentrations in mineral dust of unknown composition. As a qualitative proof-of-principle, the work presented is sufficient for publication. However, there are serious deficiencies in the details of the experiments, the experimental design, interpretation of the results, and as a result the claim of quantitative results is not supported by the evidence presented.

I recommend publication with major revisions. Either the description of the experiments

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and proof of the calibre of the design must be enhanced, or the manuscript should be re-written to indicate that it is a proof-of-concept qualitative approach. The concerns I have are discussed below.

1. Pulsed laser LII is a well-researched technique. There is only one reference to the pulsed LII literature (Michelsen et al., 2007 – note spelling of Michelsen), while there are several references to cw-LII literature, which are only partially relevant to the experimental technique employed. An excellent review of pulsed laser LII is Schulz et al. 2006 [1]. The authors discuss using a 1064nm / 532 nm Nd:YAG pulsed laser with pulses of 5-10 ns duration. However, no mention is made of the laser beam spatial profile (Gaussian, tophat, ...), the laser fluence (energy per unit area), the repetition rate (single shot, 10 Hz, 20 Hz, ...), etc., all of which are critical to the performance of an LII instrument. Ref. [1] discusses these points in detail. The sample volume is not defined (what region is the PMT imaging). Presumably with the use of the integrating sphere, the PMT is recording signal from all locations between the sample inlet and exit from the sphere. As such, unless the laser is used in single-shot mode, it is likely that the particles are being illuminated multiple times with the laser as they traverse the path across the sphere. This will change the response as the particles are altered with each successive laser pulse. The authors also do not describe what laser fluence is being used, nor how the optimum fluence was determined. Note that there are many approaches to pulsed laser LII, including those that do not raise soot/BC to its sublimation temperature. As such, not all employ the “relatively violent process” referred to by the authors and also primarily employed by Michelsen et al. (2007). At low fluence, the LII signal is proportional not only to the BC concentration, but also to the temperature of the BC particles. Unless particle temperature is measured (i.e. with two-colour LII) it is not possible to assess concentration from peak signals alone. At moderate fluences, the particles are raised to just below sublimation temperatures, so that the signal is no longer varying as strongly with temperature, but the two-colour approach is still preferred. At higher fluences, the particles are being partially destroyed through sublimation, but there can be a relationship between the peak signal and concentration.

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At very high fluences, the particles may be completely sublimated. With no discussion of the fluence employed, it is impossible to assess the quantitiveness of the results presented. As the fit temperature is reported as 4300 K, it is apparent that at least a moderate fluence was employed. However, there is no way to know if this was 1x, 2x, 5x, or 10x the threshold required to reach 4300 K (i.e. more fluence will not increase the particle temperature, but will destroy more of the particle).

2. There are references illustrating that pulsed laser LII may be used to measure BC in atmospheric air in the presence of many other aerosol species [2, 3]. These demonstrate the selectivity of the pulsed LII technique to BC with many potential interfering species also present. Some discussion of the current results in light of the prior atmospheric literature for pulsed LII measurements of aerosols is required. Is there any reason to expect significant incandescence from species other than BC? High LII signals are produced by refractory materials that remain solid up to 4000 K and have high absorption/emission characteristics. While mineral dust may have refractory materials present, would these be expected to absorb and emit effectively? What are the optical properties of the other materials present?

3. The discussion of the results does not mention the structure of the black carbon particles as a contributing factor to the interpretation of the LII signals. There will be size and morphology issues. Pulsed laser LII works well for BC particles that are in the Rayleigh regime (size is small relative to the wavelength of the laser). For freshly emitted soot, the particles are fractal aggregates with a very open structure, such that the characteristic dimension of importance to LII is the diameter of the primary particle (15 – 50 nm; typically 20-30 nm), which is well within the Rayleigh limit for both 532 and 1064 nm irradiation. However, aged soot particles, such as those that may be found in mineral dust, typically have a more collapsed structure, and in this compact form may not be within the Rayleigh regime. If not in the Rayleigh regime, the quantitative aspect of LII is no longer possible. Another aspect of morphology is that the aggregates may have subsequently agglomerated. The LII technique cannot distinguish between

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aggregates and agglomerates, and agglomerates are likely to behave similarly to compact aggregates. Looking at Fig. 3, the long decays (typically less than 1 microsecond for freshly emitted soot) are indicative of a lower specific surface area, associated with larger primary particles, compact aggregates, or agglomerated soot particles.

4. The heating of the samples does not assure that the particles are BC. It would have been interesting to heat the particles under an inert atmosphere to drive off the volatiles and observe whether there was an effect on the remaining sample. In this case, the BC should have remained as it was. The results as presented only prove that the incandescing species was mostly removed by prolonged heating in an oxidizing atmosphere. While it is likely that the incandescing particles were BC, this alone is not proof of their composition. As another control experiment, one could mix carbon black with another species (such as silica) in similar ratios to those found in the dust samples and subject to the same heating protocols (inert and with air) and observe the effect on the LII incandescence.

5. The discussion of mass absorption cross-sections (MAC) should include previous assessments performed using pulsed laser LII [3]. Ref [3] illustrates that MAC can vary widely depending upon the composition of the aerosol, attributing it to coatings on the BC particles. Therefore, a single MAC value may not be appropriate for quantitative assessment of the results.

6. In Fig. 3, the peak LII signal occurs completely after the end of the laser pulse. What is the physical explanation for this unusual behaviour? Normally, the peak heating and peak signal in pulsed laser LII occurs before the end of the laser pulse.

7. The enhancement of the LII signal observed at 110 C could be due to charring of organic carbon compounds present in the mineral dust samples. This effect is often noted in thermo-optical analysis of samples to assess organic carbon to elemental carbon content [4]. There is no possibility of generating an LII response from organic molecules that are removed by the 250-350 C heating. This speculative statement

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should be removed.

8. What is the significance of the faint “L” shape noted in the optical images of the particles? It is mentioned in the text and the caption, but serves no purpose. In the analysis of the images, there is no mention of what lasing period / number of pulses the particles were exposed to. There is a comparison to the results of Michelsen et al. (2007) but it should be noted that Michelsen et al. performed carefully controlled and well-documented experiments. Is the increase in particle number and shift to smaller sizes the result of the creation of new particles, or simply a de-agglomeration process? What evidence do the authors have for the creation of new particles?

1. Schulz, C., Kock, B. F., Hofmann, M., Michelsen, H., Will, S., Bougie, B., Suntz, R., Smallwood, G., “Laser-induced incandescence: Recent trends and current questions,” *Applied Physics B: Lasers and Optics*, 83, 333-354, 2006.

2. Liggio, J., Gordon, M., Smallwood, G., Li, S. M., Stroud, C., Staebler, R., and Brook, J. R., “Are emissions of black carbon from gasoline vehicles underestimated? Insights from near and on-road measurements,” *Environmental science & technology*, 46, 4819-4828, 2012.

3. T. W. Chan, J. R. Brook, G. J. Smallwood, and G. Lu, “Time-resolved measurements of black carbon light absorption enhancement in urban and near-urban locations of Southern Ontario, Canada,” *Atmospheric Chemistry and Physics*, 11, 10407-10432, 2011.

4. Cavalli, F., M. Viana, K. E. Yttri, J. Genberg, and J-P. Putaud, "Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol," *Atmospheric Measurement Techniques* 3, 79-89, 2010.

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