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Atmospheric Measurement Techniques Discussions

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.

L. Ma et al.

jon.thompson@ttu.edu

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(author response prepared by Lulu Ma and Tingting Cao)

Anonymous Referee #2 Received and published: 28 November 2013

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,

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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 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

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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. At very high fluences, the particles may be completely sublimated. With no discussion of the fluence employed, it is impossible to assess the quantitativeness 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).

Author response: We appreciate your time and valuable comments on our experiments and results. For some references to LII technique, we deleted SP2 and cw-LII literature and added some about pulsed laser LII. You should see them in revised paper.

Some more details about the laser beam: spatial profile is flat-top and repetition rate is 20Hz. For laser fluence, we applied laser with several different energies (eg., 13 and 19 mJ), so there was not just one fluence. However, we do know the diameter of the laser beam, which is around 4.5 mm.

The laser power/energy was determined by measuring LII signal emitted from fresh kerosene soot. The LII signal per mass basis appeared to reach the highest value at around 19mJ.

Due to the fact the LII beam volume is < 0.01% of the sphere volume, most samples likely passed through the LII cell without being illuminated. And particles were not being illuminated multiple times even though we didn't use single shot laser.

The energy of laser beam was set at 19 mJ. This value was chosen by measuring LII signal of fresh kerosene soot in the energy range between 0.8 and 23 mJ. The LII signal appeared to reach the highest value at around 19mJ.

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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?

Author response: EDS analysis showed that aluminum, calcium, carbon, iron, magnesium, oxygen, silicon, and potassium were elements containing in dust samples (see fig 1,2 of other reviewer comments). Atomic percentage of C dropped from about 0.2 % to about 0.05 % after heated to approx. 900 C. Unfortunately, it is difficult to obtain an accurate concentration of carbon (reason has been describe in paper). The result might indicate that no drastic reaction of metals was observed during heating. Among these materials, only carbon could be oxidized during heating emitted into the air, which would results in a mass loss for the sample. For all other materials, they could also be oxidized, but will be still be in the samples, producing LII signals from laser illumination. No big different of percentage concentrations of other metal materials was observed, which may also indicates no drastic reaction happened on these metal elements. So from the results of SEM-EDS, we still insist the LII signals were from Carbon instead of other materials.

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

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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 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.

Author response: We use soil dust as sample, the internal structure of which might be different from soot. The particle of soil dust is obviously larger than single soot particles. However, a quantitative relationship between LII signal and concentration was still found. We also use condensation particle counter to measure number concentration of particles and confirm the relationship.

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.

Author response: The exact composition is very complex and difficult to determine, but based on the EDS result above, we think the heating process can only removes

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carbon-containing materials away. It may not be black carbon only, but should be carbon-containing materials (elements or organic carbons and carbonates).

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.

Author response: Both results in Figure 2 were from our experiment. We compared the LII signal we got from dust samples with that from fresh soot. And the reason we used MAC value in the literature was because we used fresh soot (with no coatings) in our experiment, and think it is reasonable for quantitative assessment of results from soot. And for dust samples, we did use PSAP and mass concentration monitor for MAC value calibration.

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.

Author response: Pulsed laser at a frequency of 20 Hz was used. Each pulse only lasted 5 ns. This has been explained in the description of figure 3.

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 should be removed.

Author response: We appreciate your explanation for the signal change at 110 C. And we found another reference talking about the thermal separation of carbon soot. And in

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revised paper, we think it is possible the precombustion of carbon soot in dust samples caused a LII signal loss by the 250-300 C heating (Cachier, 1989)

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?

Author response: The faint "L" shape was used to find the same location for particle size distribution because it did not move. In our experiment, we use soil dust as sample. The composition of soil dust is different from soot. Though we observe small particles appeared after laser illumination, the internal mechanism of this phenomenon needs further study.

Response Reference:

Cachier, H; Bremond, MP; Buatmenard, P.: Thermal Separation of Soot Carbon, Aerosol Sci. Technol., 10(2), 358-364, 1989.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 5173, 2013.