Response to reviewer #2

We thank the reviewer for his insightful and constructive comments/suggestions, and revisions on our manuscript. Wording and grammatical changes were adapted and included in the revised version of manuscript. More substantive comments are addressed point-by-point below.

1. **The experiment is well designed but could benefit by testing the spectroscopic model with a few constructed mineral mixtures with known weight percent constituents. Seems like some lab prepared mixtures of these mineral components and asphalt with known weight percents could be used to test the overall accuracy of the SSD spectral model. They could also be used to test the sensitivity of XRD to clay species. This seem like a necessary step to demonstrate the effectiveness of the spectral model.**

Response:

We understand the request, but it is impractical to have a standard proportionally mixed dust samples which include several natural dust-forming minerals for the purpose of XRD and IR comparison. XRD has been proven to be one of the most important analytical approaches used in the qualitative and semi-quantitative study of crystalline samples, and the calculation results for IR has been tested in many past studies and shown to be in a good agreement with the standard (physical) mixture of minerals. Additional details are provided here and we have included additional clarification in the revised manuscript.

As it is already noted in the paper's text, XRD has been used as a common, reliable technique to obtain mineralogy and semi-quantitative phase abundances for atmospheric dust samples (e.g., Caquineau et al., 1997; Nowak et al., 2018). Also, many studies have employed radiative transfer (RT) to model reflectance spectra of synthetic or laboratory mineral mixtures, validating the derived abundances. For example, Robertson et al., (2016) demonstrated that physical mixtures of clay and sulfate at varying abundances were accurately determined (within 5 %) using a Hapke RT model. Another study from Poulet and Erard (2004) showed that the mineral abundances derived using nonlinear spectral mixing are accurate to within 5-10 % for the laboratory mixture of pyroxenes, olivine, plagioclase, with various particle sizes.

Moreover, there is a large body of research that show the mineral abundances derived from XRD are in good agreement with IR reflectance spectra derived abundances (e.g., Thorpe et al., 2015; Pan et al., 2015; Leask and Ehlmann, 2016). For example, Leask and Ehlmann (2016) performed measurements on 15 rock samples (with various particle size) collected from Oman, and they found that VSWIR reflectance spectroscopy paired with linear spectral unmixing yields quantitative mineral abundance estimates that are consistent (within 10-15 %) with XRD abundance estimations.

These prior studies have validated the approach for mixtures of a few minerals and the goal of our study is to test this on natural dust samples that are a complex mixture of many natural minerals. The number of mineral phases in these samples varies from six to nine individual minerals, therefore, it is nearly impossible (and is impractical) to create complex physical models in widely varying abundances as observed in our samples for the purpose of comparison.

For additional clarification we added the following sentence to the introduction section of the manuscript's text, after the line which explains about Robertson et al., (2016) testing the accuracy of RT models through comparisons with physical mixtures.

"Multiple past studies have shown that the mineral abundances (for rocks and rocking forming fine grained mineral samples) derived from visible and infrared reflectance spectra are in good agreement with minerals abundances that are obtained using XRD (e.g., Pan et al., 2015; Thorpe et al., 2015; Leask and Ehlmann, 2016). For example, Leask and Ehlmann (2016) performed measurements on 15 rock samples (with various particle size) collected from Oman, and they found that VSWIR reflectance spectroscopy paired with linear spectral unmixing yields quantitative mineral abundance estimates that are consistent (within 10-15 %) with XRD abundance estimations."

References (* represents the new references that have been added to the manuscript)

Caquineau, S., Magonthier, M. C., Gaudichet, A., and Gomes, L.: An improved procedure for the X-ray diffraction analysis of low-mass atmospheric dust samples, European Journal of Mineralogy, 9, 157-166, 1997.

*Leask, E. K., Ehlmann, B. L., and Ieee: Identifying and Quantifying Mineral Abundance Through VSWIR Microimaging Spectroscopy: A Comparison to XRD and SEM, 2016 8th Workshop on Hyperspectral Image and Signal Processing: Evolution in Remote Sensing (Whispers), 5, 2016.

Nowak, S., Lafon, S., Caquineau, S., Journet, E., and Laurent, B.: Quantitative study of the mineralogical composition of mineral dust aerosols by X-ray diffraction, Talanta, 186, 133-139, 10.1016/j.talanta.2018.03.059, 2018.

*Pan, C., Rogers, A. D., and Thorpe, M. T.: Quantitative compositional analysis of sedimentary materials using thermal emission spectroscopy: 2. Application to compacted fine-grained mineral mixtures and assessment of applicability of partial least squares methods, Journal of Geophysical Research-Planets, 120, 1984-2001, 10.1002/2015je004881, 2015.

Poulet, F. and Erard, S.: Nonlinear spectral mixing: Quantitative analysis of laboratory mineral mixtures, Journal of Geophysical Research-Planets, 109, 12, 10.1029/2003je002179, 2004.

Robertson, K. M., Milliken, R. E., and Li, S.: Estimating mineral abundances of clay and gypsum mixtures using radiative transfer models applied to visible-near infrared reflectance spectra, Icarus, 277, 171-186, 10.1016/j.icarus.2016.04.034, 2016.

*Thorpe, M. T., Rogers, A. D., Bristow, T. F., and Pan, C.: Quantitative compositional analysis of sedimentary materials using thermal emission spectroscopy: 1. Application to sedimentary rocks, Journal of Geophysical Research-Planets, 120, 1956-1983, 10.1002/2015je004863, 2015.

2. **Amorphous "humps" in XRD patterns can be used to qualitatively assess samples for the presence of non-crystalline phases and they should be re-examined for this evidence.**

Response: We thoroughly examined all samples' XRD plots, and we do not observe any discernible "humps" or broad features that could be attributed to non-crystalline phases.

3. **Modifying the statement "To date, VNIR/SWIR spectroscopy has not been used to study natural dust particle mineralogy; however, it can provide quantitative measurements and identify both amorphous and crystalline phases (Clark, 1999)".**

Response: We modified the statement to "To date, very limited studies have used VSWIR to determine natural dust particle mineralogy (e.g., Reynolds et al., 2020); however, it can provide quantitative measurements and identify both amorphous and crystalline phases (Clark, 1999)".

We added the following reference from Reynolds et al., (2020), to the reference section.

Reynolds, R. L., Goldstein, H. L., Moskowitz, B. M., Kokaly, R. F., Munson, S. M., Solheid, P., Breit, G. N., Lawrence, C. R., and Derry, J.: Dust Deposited on Snow Cover in the San Juan Mountains, Colorado, 2011-2016: Compositional Variability Bearing on Snow-Melt Effects, Journal of Geophysical Research-Atmospheres, 125, 24, 10.1029/2019jd032210, 2020.

4. **Map needs a scale in km. Are the lats and longs for the image corners?**

Response: Scale in km is added to the map in the revised manuscript. The statement "Shown latitudes and longitudes are the coordinates for the corners of the map", was added to the caption of Figure 1.

5. **Why not use the "JADE" database? Illite seems like a pretty common mineral. Explain.**

Response: Our intent was not clearly conveyed as both reviewers misunderstood this discussion.

While using the DIFFRAC.EVA, software to perform the XRD evaluation, we compared the dust sample patterns to a reference database of minerals to identify peaks in the sample. The illite reference pattern is included in the software database and this mineral was readily and confidently detected. However, we were unable to export the reference illite data (e.g., text or XY format files) from the DIFFRAC.EVA software in order to plot it in Figure

2 and demonstrate it as a standard reference. Therefore, we used two highly-cited published studies (Gualtieri (2000) and Drits et al., (2010)) as references for the location of the illite peak.

We have revised the text to read:

"The identification of the illite peak in Fig 2 uses data from the published literature such as from Gualtieri (2000) and Drits et al., (2010). While this peak pattern was available in the DIFFRAC.EVA software we were not able to export the reference patterns in order to show them in Fig 2. We used the AMCSD database for other minerals shown in Fig 2, but this database does not include a pattern for illite."

6. **Why weren't clay separations done? Explain.**

Response: The following statement was added to the Sect. 2.2 X-Ray Diffraction (XRD) to clarify why clay separation were not done:
"Because the volumes of dust samples were low, XRD sample preparation specifically for clay minerals was not conducted. Also, we could not follow sample preparation developed for low mass atmospheric dust samples (Caquineau et al., 1997) due to a lack of access to specialized equipment."

7. **Add a few sentences that discuss the lower thresholds for semi-quant XRD. Can it detect kaolinite at less than 5wt%? This might help explain differences between what spectroscopy and XRD detect.**

Response: The following statement was added to Sect. 2.2 X-Ray Diffraction (XRD) to clarify the XRD detection limit:
"S-Q abundances made from the diffraction measurements are derived from relative proportion of minerals (weight percentage %) in the sample that should add up to 100 %. Given that the XRD is less effective at detecting and quantifying poorly crystalline minerals and amorphous phases (Moore and Reynolds, 1997), the obtained abundance results for other existing well crystalline minerals can be overestimated. Past studies reported a detection limit of generally < 2 % for well crystalline minerals and an uncertainty of approximately ±10 % related to XRD mineral quantification. (e.g., Bish and Chipera, 1991)."

We added the following reference from Bish and Chipera, (1991), to the reference section.

Bish, D. L. and Chipera, S. J.: Detection of Trace Amounts of Erionite Using X-Ray-Powder Diffraction - Erionite In Tuffs of Yucca Mountain, Nevada, And Central Turkey, Clays and Clay Minerals, 39, 437-445, 10.1346/ccmn.1991.0390413, 1991.

8. **In the figure caption state that illite (I) was not in the XRD database.**

Response: Please refer to the response to point #5 above.

9. **I'm impress if you have enough halon around to press your own calibration standard. More likely this is a Spectralon calibration plate.**

<u>Response</u>: The reviewer is correct and we replaced the word "halon" with "Spectralon".

10. **Where the spectrum further corrected to absolute reflectance to remove the weak spectral signature of the spectralon 2.1 μm feature? If not explain why not?**

<u>Response</u>: Only figure 3 is presented as relative reflectance. Both Figure 6 and 7 are single scattering albedo (SSA). The reviewer correctly pointed out that we should update the relative reflectance to absolute reflectance. Following Kokaly et al., (2017) (or https://crustal.usgs.gov/speclab/data/HTMLmetadata/README/content.htm),

$R(\lambda) = R_{rel}(\lambda) * R_{Spectralon}(\lambda)$, (Eq.1)

(Where $R(\lambda)$, $R_{rel}(\lambda)$, and $R_{Spectralon}(\lambda)$ are absolute, relative and Spectralon reflectance), we converted samples' spectral measurement ($R_{rel}(\lambda)$) to absolute reflectance ($R(\lambda)$). The final manuscript will include updated figures. While further correcting the spectrum to absolute reflectance yielded better modelled fit for some samples, it had no significant influence on the final mineral abundances or our conclusions.

11. **There is no spectral evidence of illite in either of these three sample spectra. Sample S15's spectrum lacks a 2.35 μm absorption that should be present if illite were present. There is no convincing spectral evidence of illite in this sample based on its VSWIR spectrum.**

<u>Response</u>: In order to show the unique illite absorption feature near 2345 nm we are including a different sample in Figure 2 where this feature is more obvious. This will be provided in the revised manuscript.

12. **poorly stated reason. More like we show only that portion of the spectra between 1350 and 2500 microns to concentrate etc.**

<u>Response</u>: We replaced the statement "We truncated all spectral plots at 1350 nm in order to focus on the above 1350 nm spectral range with the strongest features. These samples do not include iron oxides, therefore exclusion of the spectral range from 350 to 1350 nm will not miss any major mineral components." with the following statement for the purpose of clarification:

"Since we did not see absorption features attributed to iron oxides in these samples, we truncated all spectral plots at 1350 nm in order to focus on spectral range above 1350 nm with the strongest features. Therefore, exclusion of the spectral range from 350 to 1350 nm will not miss any major mineral components."

13. **How was the absence of iron oxide/hydroxide mineral determined? Were they not identified by XRD? No observed absorptions in the visible? Some of the "dark" grains in Fig. 4a look like opaques usually attributed to Fe-bearing minerals if these are not grains of asphalt. Could it be that the concentration of Fe oxide/hydroxides in these samples is just below the XRD detection threshold? What is that threshold? Some discussion is needed on this topic, as a few hundred ppm hematite or**

goethite stains rocks red or brown. Is doesn't take much of these minerals in dust but can have a profound effect on radiative forcing of the atmosphere. That is why we are mapping them with EMIT.

Response: The color of the Ilam dust samples is gray. There are no samples with red or brown color. We thoroughly inspected all of the samples, in particular in the wavelength range between 350 to 1250 nm, and observed no spectral signature attributed to iron oxide/hydroxide minerals. XRD also showed no peaks related oxide/hydroxide minerals. The dark grain materials shown with optical microscopy (Fig. 4a) are attributed to asphalt as it was confirmed by reflectance spectroscopy (Fig. 6b, 6c, Fig. 7a, and Fig. 9).

14. **They might be glass (in figure 4, from optical microscopy).**

Response: Please see the response to point #2 above.

15. **Any supporting reference for this decision (why wet measurements were performed)?**

Response: This method provides more accurate size distributions. We added Hartshorn et al., (2021) to the manuscript, as the supporting reference of why we selected wet measurement.
We added the following reference from Hartshorn et al., (2021), to the reference section.

Hartshorn, E. J., McDonald, E. V., Weir, W. B., Sweeney, M., Houseman, S. M., Lacey, T.: An Integrated Model Combining UAS Imagery and PI-SWERL for Evaluating Intra-Landform Dust Emission Variability, Report Prepared for U.S. Army Corps of Engineers Engineer Research and Development Center Cold Regions Research and Engineering Laboratory, 2021.

16. **I'm having trouble see how the mode for sand is 3%.**

Response: The mode for sand was double-checked and the reviewer is correct. In order to avoid confusion, we have changed to the mean values for each size range and show these with a new annotation on the ternary diagram.

17. **Add a sentence or two that justifies this assumption (line 227, in initial manuscript). What part does the assumption of a uniform grain size play in the overall accuracy of the spectral modeling? Of course, this assumption may be valid given the very fine-grained nature of dust.**

Response: We revised the sentence as follows to justify our assumption.
"These spectra are shown in Appendix B (Fig. B1). Most library minerals used were in the grain size range < 150 µm. Our samples have narrow grain size range (Fig. 5) so that our model assumes all components have the same grain size and does not allow this to vary as a free parameter."

18. **The biggest discrepancy is the inverse spectralon absorption at 2.1µm. This needs to be discussed. The hump at 2.1µm is from a spectralon absorption. It would disappear if the dust spectra were corrected to absolute reflectance as the USGS spectral library spectra are.**

Response: Please see the response to point #10 above.

19. **Is this weight % or volume %. Please clarify in the (Fig. 8) caption.**

Response: Weight percentage (wt. %) was added to the caption for figure 8.

20. **I don't see a "good" spectral model fit to XRD for the checkmarked samples unless +/- 5wt% calcite is "good." Also, there is no hint of actinolite spectrally in some checkmarked samples. How can the match be "good" (caption for Fig. 10)?**

Response: The samples displayed with check marks (in Fig. 10) had a spectral fit that was relatively well modelled based on our visual evaluation and a low RMSE. For example, Fig 6a shows SSA for a good spectral fit. We assumed the samples with a good spectral fit produce relatively accurate minerals abundances and selected them for the purpose of comparison with XRD derived abundances as discussed in Section 3.2.

We revised the statement in the caption for figure 10 for the purpose for clarification:

"Figure 10. Bar charts show XRD (top) and SWIR (bottom) normalized abundances after removing the transparent minerals. Those samples with check marks had relatively well-modelled spectral fit (e.g., Figs. 6a and 6b) as described in the text, and are used for subsequent comparison as described in Sect. 3.2."

21. **An amorphous hump for the organic component of the asphalt should show in the XRD patterns. Quantifying this might be difficult unless standards with known weight percent organics where used to derive a calibration for the intensity of the hump.**

Response: Please see the response to comment number 2. Also, as we discussed in the manuscript we were interested in minerology and not the manmade constituents present in the samples.

22. **Certainly, dark asphalt may suppress the scattering of photons and its effect at low abundance might confound Hapke modeling when it is present even at low abundances. But the oxidized asphalt spectrum shown in fig. 7a has 70 % reflectance in the SWIR. This is pretty bright so shouldn't be spectrally dominant the way fresh unoxidized dark asphalt would.**

Response: The reviewer has misinterpreted Figure 7. The spectra for asphalt and tar shown are presented as single scattering albedo. They have absolute reflectance values lower than 23 %, contributing as dark agents in dust samples.

To clarify about asphalt reflectance value, we added the following statement to Section 4.3.

"It is good to note that the reflectance values for asphalt and tar in the USGS library (Kokaly et al., 2017) are less than 23 %."

23. **This is not quite true in my experience. I routinely use spectroscopy to gauge the crystallinity of kaolinite and alunite. I would say spectroscopy is sensitive to both molecular bonding and in many cases crystalline order.**

Response: We replaced the statement “SWIR spectroscopy, being sensitive to molecular bonding rather than crystallography, provides additional information.” with:

“SWIR spectroscopy, being sensitive to molecular bonding, provides additional information.”

24. There is a spectrum of this in the USGS library labeled polystyrene.

Response: As shown in the image below, the Styrofoam materials we measured (Sadrian et al., 2021) are distinct from the polystyrene spectra from USGS library (Kokaly et al., 2017).

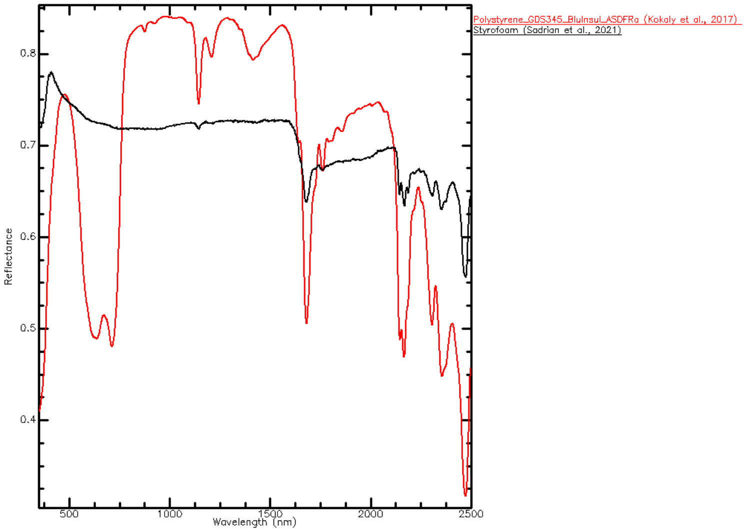

Image shows the differences between the polystyrene spectra (red line) exported from USGS library (Kokaly et al., 2017) and the Styrofoam spectra (black line) that Sadrian et al., (2021) measured in the lab.

25. Terms:

We replaced “VNIR/SWIR” with “VSWIR” in whole manuscript, and "full spectral range" with "combined VSWIR and LWIR ranges" in Sect. 4.5.