

Responses to reviewer #1

We thank the anonymous reviewer for their valuable and constructive comments/suggestions on our manuscript. We have revised the manuscript accordingly and please find our point-by-point responses below.

- 1. This is a methodology study and should have a standard proportionally mixed samples for comparison. So, the results for the mineral percentages based on combined XRD and IR methods may still not be convincing. At least, the calculation results have to be tested by the standard mixture.**

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 manuscript, 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 rocks 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 sizes) 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. The calculation of the mineral contents based on the XRD patterns of the natural samples should be careful, as the peaks may be the overlapped results of several different minerals, such as the peak for the kaolinite might contain d(002) peak of chlorite, etc.**

Response: Without special sample preparation XRD might miss detecting some clay minerals, whereas VSWIR spectroscopy is a complementary technique used both to obtain new phases (such as amorphous phases or partly crystalline clay minerals that are probably not detected by XRD) and to confirm the phases that are already identified by XRD. Chlorite has diagnostic absorption features in VSWIR, due to several iron absorption bands between 400 to 1100 nm, and characteristic complex doublet absorption near 2330 and 2390 nm, which makes it readily identifiable in this spectral range (VSWIR) (e.g., King and Clark, 1989; Kokaly et al., 2017). We thoroughly inspected all of the samples' IR spectra (specifically for clays such as chlorite and various iron oxides) and we could not find spectral signature attributed to chlorite in these samples. Therefore we concluded the peak for kaolinite does not contain d(002) peak of chlorite, and is solely attributed to kaolinite.

References

Clark, R. N., King, T. V. V., Klejwa, M., Swayze, G. A., and Vergo, N.: High Spectral Resolution Reflectance Spectroscopy of Minerals, *Journal of Geophysical Research-Solid Earth and Planets*, 95, 12653-12680, 10.1029/JB095iB08p12653, 1990.

King, T. V. V. and Clark, R. N.: Spectral Characteristics of Chlorites and mg-Serpentines Using High-Resolution Reflectance Spectroscopy, *Journal of Geophysical Research-Solid Earth and Planets*, 94, 13997-14008, 10.1029/JB094iB10p13997, 1989.

Kokaly, R. F., Clark, R. N., Swayze, G. A., Livo, K. E., Hoefen, T. M., Pearson, N. C., Wise, R. A., Benzel, W. M., Lowers, H. A., Driscoll, R. L., and Klein, A. J.: USGS Spectral Library Version 7, Reston, VA, Report 1035, 68, 10.3133/ds1035, 2017.

- 3. Should the relative proportion of different compositional groups be reported as volume percentage or area percentage or weight percentage? If it the weight percentage, some more conversion factors must be used according to the world standard such as American Standard for the XRD-based mineral identification?**

Response: XRD semi-quantitative (S-Q) abundance analysis is calibrated by mass, and calculates the weight percentage (wt. %) of the phases present in the samples. As describe in Sect 2.6, the output result for the spectral modelling is mass fractional abundance for each component in the sample. The mass fraction is also known as the

mass percentage (mass %) and is equivalent to the weight percentage. We added wt. % to the caption of figure 8 to clarify the units for XRD S-Q measurements.

- 4. Line 104-106: It is stated “Although there were no standard reference patterns in the AMCSD dataset to show the match peak for illite, we detected this mineral in S11 based on the visual assessment and past published data on the location of illite peaks”. Does it mean that the “illite” mineral in the analyzed samples are the illite/smectite mixed layer with the d(001) from 10 to 15 Å, i.e., the transition between the illite and smectite?**

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."

References

Drits, V. A., Zviagina, B. B., McCarty, D. K., and Salyn, A. L.: Factors responsible for crystal-chemical variations in the solid solutions from illite to aluminoceladonite and from glauconite to celadonite, *American Mineralogist*, 95, 348-361, 10.2138/am.2010.3300, 2010.

Gualtieri, A. F.: Accuracy of XRPD QPA using the combined Rietveld-RIR method, *Journal of Applied Crystallography*, 33, 267-278, 10.1107/s002188989901643x, 2000.

5. The percentages of detected minerals measured by XRD are different from measured by SWIR. Compared with SWIR, the XRD overestimate the quartz and calcite contents, and underestimate the clay mineral contents. However, which results can we trust, XRD or SWIR?

Response: Past studies reported a detection limit of generally $< 2\%$ for well crystalline minerals and an uncertainty of approximately $\pm 10\%$ related to XRD mineral quantification. (e.g., Bish and Chipera, 1991).” Our analysis showed that SWIR reflectance spectroscopy is well-suited to identify and quantify clay phases (such as Montmorillonite) that would be missed by XRD techniques and is also a quick and effective way to survey a group of samples with little preparation. In addition, SWIR is advantageous in detecting absorption features attributed to non-mineral materials in samples (such as asphalt), as well as amorphous and partly crystalline minerals. XRD, on the other hand, can reliably identify well crystalline minerals, nevertheless, it is less effective at detecting weakly crystalline (some clays) or amorphous phases (such as manmade materials). Further, XRD can accurately detect quartz, feldspars, calcite, and amphibole in dust samples, and estimates relatively reliable abundances for them. However, SWIR could not identify these silicates and carbonates due to either not being absorbed by them or the limitations incurred by fine grain size or dark manmade materials that are present in the sample. Our results indicate that it is beneficial to use both XRD and reflectance spectroscopy to characterize natural airfall dust, because the former technique is good at identifying and quantifying the SWIR-transparent minerals (e.g., quartz, albite, and microcline), while the latter technique is superior for determining abundances for clays and non-mineral components.

Regarding reviewer’s comment, we have added the following statement to the conclusion section.

“Because quartz and feldspars are substantial fractions of total mineral abundances of dust samples (Fig. 8), we suggest the use of XRD as an initial reliable method for mineral identification and quantification. Based on our analysis, we recommend that future research include spectral measurements in both VSWIR and LWIR, as the latter spectral range can be complementary to the former and obtained abundances for SWIR-transparent minerals (e.g., quartz and feldspars). As a result, the present minerals in the bulk sample can qualitatively and quantitatively assessed by both VSWIR and LWIR, and then confidently compared with XRD determined mineral abundances.”

Reference (* represents the new reference that has been added to the manuscript)

*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.

- 6. Line 166: “The modes for each size ranges are clay ~ 6 %, silt ~ 85 %, and sand ~ 3 %.” From Figure 5, it looks that the “Sand ~ 3 %” is not correct.**

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.

- 7. The section title sequence number needs to be revised.**

Response: The section title sequence number has been revised.