

## Interactive comment on "Technical Note: Mineralogical, chemical, morphological, and optical interrelationships of mineral dust re-suspensions" by Johann P. Engelbrecht et al.

## R. Reynolds (Referee)

rreynolds@usgs.gov

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## General comments

This Technical Note provides a compendium of important mineralogic, chemical, physical properties of widely distributed materials (mostly surface soils and aeolian sediments) sampled from re-suspension in the PM2.5 and PM10 size fractions. The primary goal is to provide data that can be used to evaluate the effects of atmospheric dust primarily with respect to radiative forcing and human health. The measurement of radiative properties during re-suspension and comparison with compositional parameters provides important information relating dust mineralogy to optical properties (Fig. 4.5-1). The SEM micrographs and accompanying EDS spectra are of excep-

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tional quality and provide a helpful view into typical mineralogic complexity of PM2.5 particles. The comparisons among SSAs, iron, and clay minerals invite collaborative discussions about alternative explanations for the observed relations.

## Specific comments.

The manuscript emphasizes the relations among iron, clay minerals, and optical properties. Fe is interpreted to mostly reside in montmorillonite on the basis of correlation of Fe and Al (p. 11). Certainly, some Fe is structurally bound in many of the clay minerals encountered in this study. But how much? A quick scan of literature and text books indicate typical structural Fe concentrations in montmorillonite and illite between  $\sim\!1$  and 7 wt %, expressed as Fe2O3. (Of course, chlorite and nontronite by classification and structure contain a lot of Fe – on the order of 8-20+ wt % Fe2O3.) Considering the samples that contain primarily rock-derived sediment (i.e., ignoring salt-/carbonate-/diatom-bearing playa samples), the correspondence between Al and Fe could also be attributed to the co-existence of ferric oxide minerals (hematite and goethite) with clay minerals, in varying relative proportions depending on factors of provenance, sorting, and pedogenesis, in some instances.

One reason for my concern (with background in iron oxides but not in clay minerals) stems from the relations illustrated in the scatter plots of Fig. S4-4. The ratios of Fe2O3 to Al2O3 for most samples (blue markers) seem to be about 0.7.

Some sleuthing on chemical analyses of clays, including "standards" used for reflectance spectroscopy (http://speclab.cr.usgs.gov/spectral.lib06/ds231/datatable.html ) reveals the following Fe2O3/Al2O3 ratios:

illite: 0.07-0.29

montmorillonite: 0.04-0.28

kaolinite: 0.01-0.04

chlorite: 0.48

These ratios are based on the following analyses for Fe2O3 wt %:

Illites: 1.6, 6.4, 4.99

Montmorillonite: 5.8, 3.2, 3.5, 1.4, 1.75, 1.2, 3.85

Chlorite 8.3

In many of this study's samples, there seems to be a large excess of chemical Fe2O3 that cannot represent structural Fe in clays.

I suggest that the authors reconsider their interpretation that the correspondence between Fe and Al is produced primarily by structural Fe in clay minerals. I suggest instead that - except perhaps for the samples low in Fe and Al - the "excess Fe" is better explained by the presence of the minerals hematite and goethite these sediments, beyond their abundance attributed by the authors. The reason that these ferric oxides have not been commonly noted is that researchers have not looked closely enough for them with specialized instrumentation, which is admittedly difficult to access. These minerals appear to be common in fine-grained, rock-derived sediments worldwide. They are probably ubiquitous in sediments having hues of red, orange, and yellow. Recent work shows these ferric oxides to be commonly nano-sized (<50 nm) and to occur as discrete particles within and on clay minerals and in other occurrences in the same sample. They are revealed by certain magnetic properties and Mössbauer spectroscopy especially at 4.2K (liquid He temperature) because these ultrafine minerals are magnetically ordered at very low temperatures but not at room temperature. The nano-ferric-oxide minerals can be observed (and confirmed as Fe oxide) under very high resolution SEM with EDA beam diameters on the order of a few 10s nm. I suggest that the dust community consider the following: The radiative properties of at least many samples (standards and natural) described as containing Fe-bearing clays are actually strongly controlled by the presence of ferric oxide minerals, many of which are nano-size (Reynolds et al., 2014a, 2014b; Moskowitz, manuscript in review). This distinction is no small matter with respect to modeling the radiative effects of dust in

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the atmosphere and on surfaces of ice and snow.

The authors similarly attribute the correspondences between Ti - Al and Mn - Ti to residence of Ti and Mn in clays. It appears to me that much of the Ti and Mn are associated with Fe(-Ti) oxide minerals such as ilmenite (usually <5 wt %) and (or) the generally more abundant ferromagnesium silicates, as identified in many samples.

Issues of "long-range transport" [not defined] of dust particles "typically < 9 microns": A body of work indicates the presence of larger particles transported at regional (10s to many 100s km) and global scales (many 1000s km). A few articles on the topics are: Beltzer et al., 1988; McTainsh et al. 1997; Middleton et al., 2001; Alastuey et al 2005, Chan et al., 2005; Lawrence and Neff, 2009; Neff et al., 2013; van der Does et al., 2015.

Particles >PM10 certainly have important effects on the Earth System through radiative properties (atmospheric and snow/ice melt), infrastructure, health (in the upper respiratory system if not deeper), and fertilization.

Was there any black carbon in any of the samples that might have enhanced measured radiative properties?

P. 2, lines 8-9. Please see Ghio et al., 2014 with respect to medical studies of biologic effects of dust on human lung cells.

One comment about presentation that I did not include in my previous "comments":

I think that the section (3.1) on samples and settings could be organized more tightly among the sub-sections (e.g., 3.1.1, 3.1.2, 3.1.3,....3.1.25). Some samples are described in adequate detail but others are very vague (e.g., "The two samples from Utah were similar to each other, both taken along a dirt road" does not convey any meaningful information and leaves open many questions—what are the local substrates; was the road graveled and (or) graded? And more. With parallelism and more consistency, Section 3.1 would be more easily read and informative.

References cited: Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., et al. (2005). Characterisation of TSP and PM2.5 at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan Dust Episode (July 2002). Atmospheric Environment, 39(26), 4715-4728. doi:10.1016/j.atmosenv.2005.04.018

Betzer, P., Carder, K., Duce, R., & Merrill, J. (1988). long range transport of giant mineral aerosol particles. Nature, 336, 568-571. Retrieved from http://www.nature.com/nature/journal/v336/n6199/abs/336568a0.html

Chan, Y.-C., Mctainsh, G., Leys, J., Mcgowan, H., & Tews, K. (2005). Influence of the 23 October 2002 Dust Storm on the Air Quality of Four Australian Cities. Water, Air, and Soil Pollution, 164(1-4), 329-348. doi:10.1007/s11270-005-4009-0.

Ghio, A.J., Kummarapurupu, S.T., Tong, H., Soukup, J.M., Dailey, L.A., Boykin, E., Gilmour, M.I., Ingram, P., Roggli, V.L., Goldstein, H.L., Reynolds, R.L., 2014, Biologic effects of desert dust in respiratory epithelial cells and a murine model. Inhalation Toxicology, 26(5): 299-309. DOI: 10.3109/08958378.2014.888109.

Lawrence, C.R., Neff, J.C., 2009, The contemporary physical and chemical flux of aeolian dust: A synthesis of direct measurements of dust deposition. Chemical Geology. 267 (1-2), 46-63. doi:10.1016/j.chemgeo.2009.02.005.

McTainsh, G. H., Nickling, W. G., & Lynch, A. W. (1997). Dust deposition and particle size in Mali, West Africa. CATENA, 29(3-4), 307-322. doi:10.1016/S0341-8162(96)00075-6.

Moskowitz, B.M., Reynolds, R.L., Goldstein, H.L., Berguo, T., Kokaly, R.F., Bristow, C.S., Iron oxide minerals in dust-source sediments from the Bodélé Depression, Chad: Implications for radiative properties of dust plumes from the Sahara and potential nutrients. In review.

Neff, J.C., Reynolds, R.L., Munson, S. Fernandez, D., Belnap, J., 2013, The role of dust storms in atmospheric particle concentrations at two sites in the western U.S. Journal

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of Geophysical Research 118, 11201-11212. doi:10.1002/jgrd.50855.

Reynolds, R.L., Cattle, S.R., Moskowitz, B.M., Goldstein, H.L., Yauk, K., Flagg, C., Berquó, T., Kokaly, R.F., Morman, S., Breit, G., 2014a, Iron oxide minerals in dust of the Red Dawn event in eastern Australia, September 2009. Aeolian Research 15, 1-13. http://dx.doi.org/10.1016/j.aeolia.2014.02.003.

Reynolds, R.L., Goldstein, H.L., Moskowitz, B.M., Bryant, A.C., Skiles, S.M., Kokaly, R.F., Flagg, C.B., Yauk, K., Berquó, T., Breit, G., Ketterer, M., Fernandez. D., Miller, M.E., Painter, T.H., 2014b, Composition of dust deposited to snow cover in the Wasatch Range (Utah, USA): Controls on radiative properties of snow cover and comparison to some dust-source sediments. Aeolian Research 15, 73-90. doi.org/10.1016/j.aeolia.2013.08.001.

van der Does, M., Korte, L., Munday, C., Brummer, G.A., Stuut, J., 2015, Lateral and seasonal trends of Saharan dust deposition along a transect over the Atlantic Ocean. American Geophysical Union Fall Meeting Abstracts A33L-0356.

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