Review of Knepp et al. (AMT-D, 2021), "Identification of Smoke and Sulfuric Acid Aerosol in SAGE III/ISS
Extinction Spectra Following the 2019 Raikoke Eruption" ***- Revised manuscript***

Reviewer: Mike Fromm

K21 have made substantial and necessary changes to their manuscript. Even though they are necessary, they are not sufficient to alter my major concerns with the paper. The root of my concerns is that their method of inferring particle composition is based wholly on the spectral slope of aerosol extinction in the visible to near-IR and that they provided no independent observational proof that wavelength-dependent aerosol extinction in this range unambiguously carries particle-composition information. K21 appropriately present the two main elements that might distinguish smoke from sulfates in their imprint on vis-NIR extinction spectra, absorption and particle-size distribution (PSD). However, a priori establishment of these two qualities is not satisfactorily made. The role of absorption is presented in the theoretical realm, embodied in Figures 3 and 5. But the confounding effect of PSD is given inadequate attention. If there is to be a single, algorithmic relation between aerosol extinction and spectral slope, it must be established that volcanic sulfates and wildfire smoke have characteristic, systematic differences in PSD. If there is no such systematic difference between smoke and sulfate, then absorption vs. scattering will rule and there should then be an unambiguous systematic difference on the spectral slope between clearly homogeneous smoke and sulfate populations. The evidence provided in K21's tabular results shows that this is not the case. If in fact PSDs between smoke and sulfate are substantively different, then this factor should be presented as an empirical determinant on the spectral-slope construct (Figure 3). However, to my reading, K21 do not make that case.

A more specific major concern I expressed in the original review relates specifically to the PSD issue. I pointed out that Thomason et al. (2021) (T21) showed that even within the superset of presumed volcanic sulfates, vis-NIR extinction spectra vary widely among diverse volcanic events. Although K21, in their response to my review, rightly argue that T21 did not consider possible composition mixes, the large range of spectral extinction variation among plumes that are almost certainly exclusively volcanic (i.e. the plumes from tropical eruptions) speaks to a very wide constraint on pure-sulfate PSD. Raikoke falls within the range of these tropical sulfate plumes (T21's Figure 8, below), hence it is a considerable challenge to argue that there is a motive for questioning the Raikoke-year's composition mix considering T21.

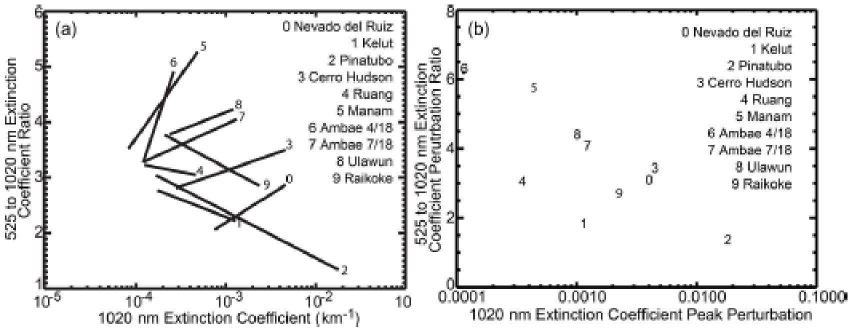


Figure 8. The "before" (left-hand point) to peak 1020 nm aerosol extinction coefficient (right-hand point) for the 10 eruptions considered in this study is shown in panel (**a**), and the differences between them (perturbations) are shown in panel (**b**).

K21 assert in their response to my review that T21's analysis has a different motive and construct as compared to K21, but extinction ratio and a spectral slope derived therefrom are inextricably linked to the same underlying determinant: small particles yield both a large extinction ratio and spectral slope.

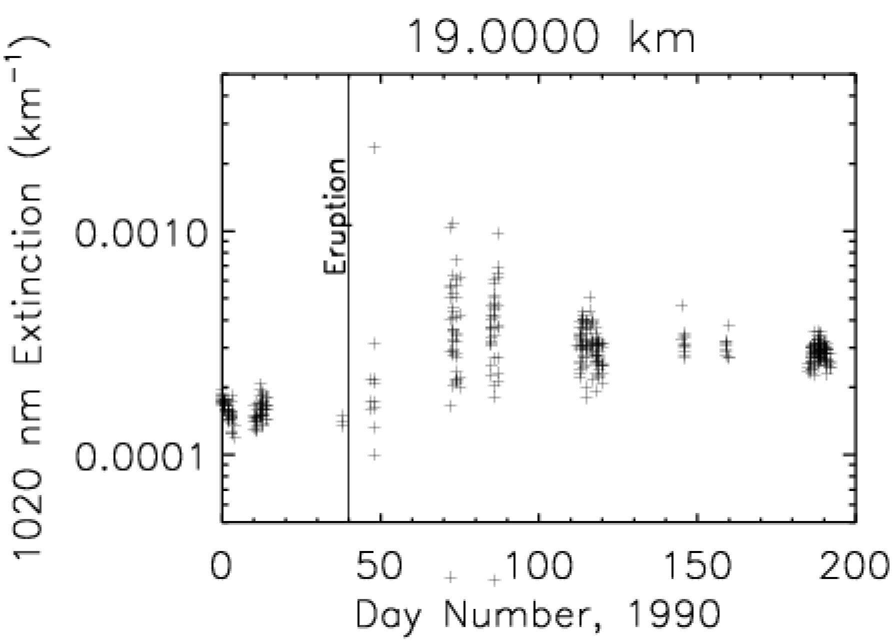
It is not logically clear why K21 make an exception for Pinatubo, when inferred volcanic sulfate PSD covers a quasi-continuous range from small to large (T21). Indeed Raikoke is situated deeply into the large-particle side of the PSD spectrum according to T21. Moreover, Thomason (GRL, 1992) characterized Pinatubo aerosols as the norm for volcanic clouds such that the "new mode" found within SAGE II extinction spectra was labelled "new" and hypothesized to be a transitional mode in volcanic sulfate-particle growth. To the extent that pyroCb smoke explained the Thomason (1992) "new mode," its relevance to the current manuscript is central to my assessment that vis-NIR extinction spectra are inadequately constrained for particle-composition inference. To wit, had K21's spectral slope algorithm been applied to Pinatubo, it is likely that SAGE Pinatubo measurements would have been classified as smoke and pyroCb smoke measurements would have been closer to sulfates.

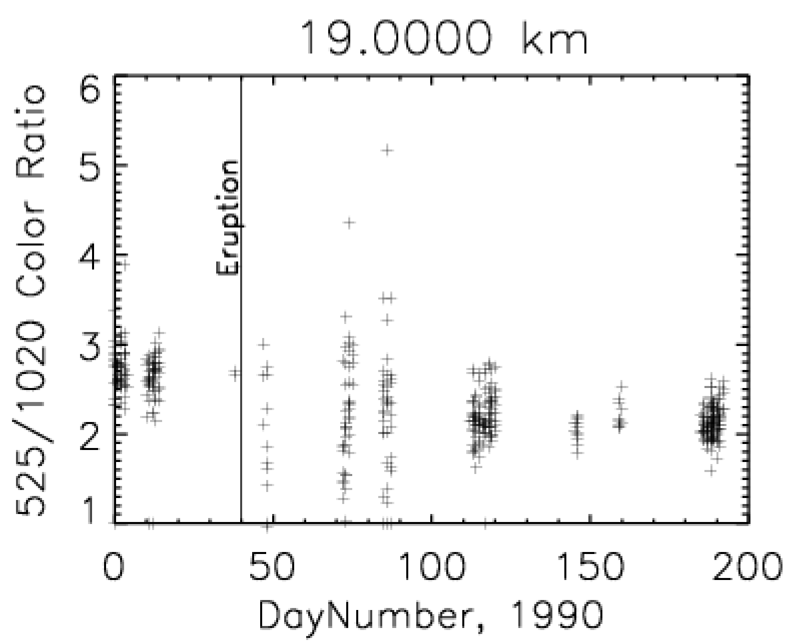
The point I made in my first review about T21 was simply that their illustration in Figure 8 was sufficient to caste large doubt on any attempt to derive a binary choice between stratospheric smoke and sulfates. T21's "perturbation" 520/1020 nm extinction ratios are all over the place, from less than background to the upper limit: unity. Roughly half the plumes have increased extinction ratios (more negative slopes, in K21 parlance) w.r.t. background, the remainder have smaller extinction ratios (less negative slope). Raikoke is in a class with three other plumes with decreased extinction ratio, each created by a tropical volcano and no question as to contributory smoke. The different motives and methods of T21 vis a vis K21 are not germane. The patterns within T21 Figure 8 map directly to K21. The fact that T21 only consider the background and peak perturbation in Figure 8 serves to clarify my point, not

diminish it. The T21 perturbation state represents extinction signals at absolute and relative maximum, a state of minimum uncertainty in the signal. Hence it is a demonstration of the optimal circumstances for assessing both microphysical evolution and composition. Hence, T21 Figure 8 shows that there is no firmer footing for questioning Raikoke's composition mix than for questioning that of any of the other three plumes in Raikoke's class.

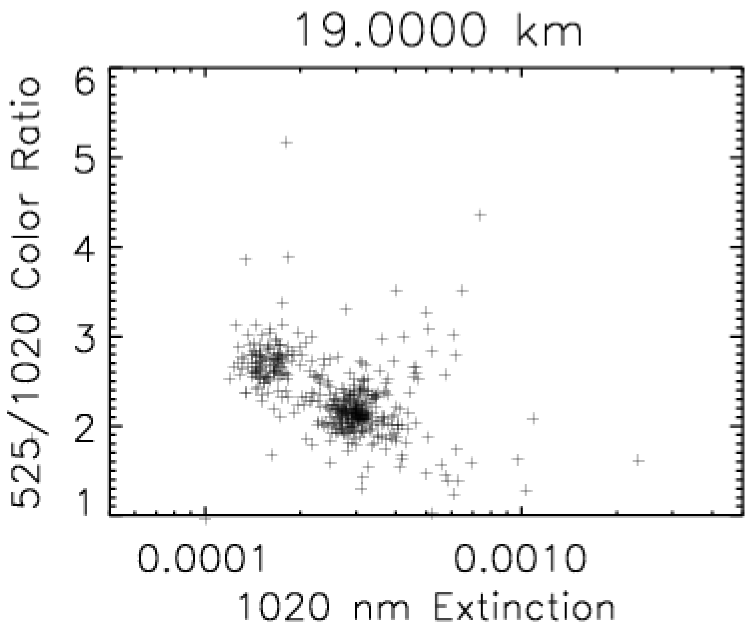
Still on the topic of T21, K21 state in the manuscript and their referee response that Pinatubo cannot be addressed with their approach. Their argument is understandable, but not compelling. Of course, particle populations of a size class that would render SAGE color ratios (spectral slopes) near unity (near zero) would inhibit interpretation. This situation is illustrative of a realm where the most appropriate finding is "uncertain." Because population-scale particle size, type, and blend fall naturally on continuous scales, so too does their manifestation in the vis-NIR extinction realm. Just as there is relatively large uncertainty in composition at the near-background level of extinction, there is also gradually increasing uncertainty as extinction ratio approaches unity. In accordance with this perspective, the natural suggestion is to define an uncertainty category in the composition algorithm rather than descoping particular volcanic plumes. The case of Pinatubo is illustrative. One can see from T21's Figure 7 that there is a point in the SAGE sampling of the young plume during which color ratios are not pegged at 1. If one considers that point in the plume's evolution, the extinction/extinction-ratio pattern closely resembles that of Kelut in T21 Figure 7 (accounting for the different ordinate scales in panel 7a and 7c) and 8. In summary, the construct presented in T21 bears two lessons for K21. One is that the Raikoke-era plume is indistinguishable from several presumably sulfate-only plumes. The other is that it is necessary for an algorithm aimed at discerning composition (or blends) needs to go beyond a smoke/sulfate binary outcome.

At the risk of "beating a dead horse," I offer one other argument related to T21. I took the example of Kelut (February, 1990) to illustrate how this volcanic cloud could suggest a smoke blend, according to K21's construct. A basic rendering of 1-micron extinction and 525/1020 extinction-ratio as a function of time are shown below. The data are version 7 SAGE II. One representative retrieval altitude (19 km) makes up this example. The extinction data are limited to profiles between 0-20°S latitude.





Next is an analysis akin to K21's Figure 4: color ratio as a function of 1020 nm extinction. It is clear that this distribution of background color ratio to perturbation color ratio is more like the two smoke examples in K21 Figure 4 and the two sulfate examples. Undoubtedly, Kelut's inarguably sulfate plume at 19 km would have been in the smoke category within the K21 construct (modified as it would be for SAGE II wavelengths). Not shown, but evident at other stratospheric altitudes up to 21 km, is this same pattern. At higher altitudes it morphs to a more K21 sulfate pattern. This is reminiscent of the altitude variation of smoke/sulfate proportion systematics presented in K21. To me this is further evidence of the weakness of the SAGE data and the K21 construct for composition inference.



In response to referee suggestions, K21 invoked additional satellite data to qualify their findings. For instance, they showed TropOMI SO2 in concert with a SAGE profile (Figure 1) deemed to sample sulfates. This was very helpful. However, it would help the reader if K21 would refer to Figure 1 and report on the algorithmic result for this profile (as they did of another example shown in Figure 19). At a glance, the 520/1550 extinction ratio at peak extinction is quite small (~6.7) in comparison to the two sulfate distributions in K21 Figure 4 (~10 being the minimum) and much closer to the two smoke examples.

They also introduced ACE-FTS gas and aerosol information. In this endeavor, they cited Chris Boone of the ACE-FTS team for a still novel aerosol-infrared spectrum construct for aerosol-type determination. While this led to improvements in the manuscript, in my opinion K21 drew a conclusion regarding the secondary and primary Raikoke plumes that fall short of convincing. For instance, K21 state that they find no ACE evidence of smoke above 20 km, using Figure 18 as an illustration. Absent though is any discussion of whether this conclusion is also informed by other ACE profiles not shown. Did K21 find, for instance, no CO or HCN enhancements above 20 km? Did they find a substantial number of ACE profiles with such enhancements up to 20 km? If so, that would bolster their conclusion. Specific to Figure 18, there is a concern with respect to the profile in which the ACE aerosol-infrared spectrum approach showed a smoke signal at 20 km (Figure 18 j,k,l). The smoke marker is at 20 km, above any CO or HCN enhancement, but centered on a huge SO2 enhancement. At a glance this appears to be confusing at best, erroneous at worst. Given that this profile is at 24N, 34E (situated on the western side of the Asian Summer Monsoon anticyclone, it may be a case of upper tropospheric biomass burning signal below the SO2 peak, and a volcanic plume above.

It should be examined more closely before a final determination, but as it stands, it is not a compelling foundation for K21's conclusion that smoke was observed up to 20 km.

Regarding the stratospheric Raikoke-season plume that ascended to 22+ km at low latitudes, what K21 refer to as the "secondary" plume, it is evident that the smoke angle and this anomalous plume height are a prime motivation for this paper; it is highlighted in the abstract. The original and revised K21 manuscript provide an unclear motivation to pursue this as smoke assisted. In the Introduction, K21 state: "The working hypothesis was that this secondary plume consisted, at least in part, of wildfire smoke." The "was hypothesized" part implies that the idea preceded K21 yet no citations are given. Also in the Introduction, they cite 3 papers on the subject of diabatic smoke-plume lofting, but none of these involve the Raikoke-season plume. I did not find any attribution of this hypothesis to the Raikoke secondary plume" cited papers. If I missed it, the authors are asked to provide the earlier sources. Otherwise, the "working hypothesis" should be claimed as their own.

Related to the above point, the original manuscript was criticized for implicating "2 major wildfires" (Abstract) as contributors to stratospheric aerosols in 2019. The criticism was that the manuscript relied on citations that provided only vague and inconsequential support for the wildfire/pyroconvection angle. I argued that the fires and pyroconvection in 2019 were not "major" in comparison to a normal pyroCb season (while acknowledging that stratospheric smoke injections were an annual occurrence). Yet the current manuscript retains these arguments. My challenge to K21, to establish a strong argument for wildfire/pyroconvection influence, went largely unmet. That challenge remains and is an essential component for convincing the reader that fires such as those in 2019 could independently bolster the argument for a wholesale pollution of the stratosphere in the Raikoke season. I have a suggestion, to look at a pyroCb season such as 2018 with SAGE data. In that year an equal number of pyroCbs occurred in the northern hemisphere as 2019, but in the absence of a volcanic cloud and the demonstrably huge smoke plumes in the NH in 2017 or the Australian plume in 2019/20. If a sizable smoke presence were to be found, it would bolster their argument that a normal pyroCb season (such as 2019's) could present a blend worth considering in the Raikoke year.