Answer to Frank Pavia (Referee)

We thank Frank Pavia for his comments and suggestions on our manuscript. We agree with most comments and modified/updated the manuscript accordingly. Below is a point-by-point reply, [our answers appear in italics].

Frank Pavia: General comments:
The manuscript by Roy-Barman et al. will be an excellent contribution to Biogeosciences, and to chemical oceanography in general. The work constitutes a novel way to estimate the mobility of mostly-insoluble elements during dust dissolution, and the findings are highly relevant to a bourgeoning literature on using Th isotopes to quantify dust dissolution and trace element inputs. The methods, data quality, and interpretations are generally sound. Before publication, there are a several points that need to be addressed, and I encourage the authors to reconsider alternate possibilities for their recommendations for the use of dissolved Th isotopes to quantify dust fluxes (see general comments below).

Specific comments:
1) I had a hard time following the REE section of the results (section 3.3.). I think this is because of the way Figure 2 is plotted. The sharp increase in REE at the start of the FAST experiment is difficult to see in Figure 2b because the t=0 and t=1 points look like they are at the same place on the x-axis. Maybe it would be good to label the t=1 point as being immediately after dust addition (if this is the case?).

Reply: *Points at t=0 (before dust addition for D and G series) are now labelled throughout the paper with crosses to be easily distinguished from points at t= 1h and latter (after dust addition for D and G series).*

Frank Pavia: It should also be clarified that the rapid increase in REE is only seen at FAST, and not at ION (unless I am having a hard time seeing this at ION because of the same plotting issue.

Reply: *At ION, we did not measure samples for t=0. The seawater composition without dust addition is given by the analysis of the "C"control series. Hence, there is also a sharp increase of the REE concentration at ION. This explanation is now given in the MS.*

Frank Pavia: This same point holds true for 232Th and Figure 3.
Reply: *For FAST, the points at t=0 are now indicated on this graph to. For ION, the comparison between the D (or G) series and the controls (C series without no dust amendment) highlight the sharp ^{232}Th concentration increase after dust addition.*

Frank Pavia: Also, page 7 line 2 suggests that
230Th/232Th ratios as a function of time are plotted in Figure 3, but I do not see them there – I would quite like to see these ratios plotted with sampling time!

Reply: *The ^{230}Th/^{232}Th ratio vs time is now show in the electronic supplement (Fig. ES3).*

Frank Pavia: 2) I'm curious from an analytical perspective, though not necessarily for the paper, where they think their high 231Pa blanks might come from, since there is so little 231Pa in nature. That said, the precision the authors achieved on such small quantities of 231Pa, in such small samples, is remarkable.

Reply: *Thank you. The high ^{231}Pa blanks came from an accidental combination of low chemistry yields for one sample set and high MC-ICPMS "machine blanks" (blank obtained by just running the dilute nitric+ HF solution used prepare the samples). At these very low signal level, it may not represent ^{231}Pa, but result from formation of polyatomic ions desorbed from the MC-ICPMS source.*

Frank Pavia: 3) I am curious about the inferred dissolution of detrital calcium carbonate in the dust mentioned in 3.6. even though this isn't the main point of the paper. This process must be occurring above the calcite saturation horizon – what is driving this dissolution?

Reply: *The seeded dust was submitted to an evapo-condensation processing in lab in order to simulate atmospheric cloud processes, as specified in 2.1. During cloud processing simulation, the pH could be very low, enabling the dissolution of calcite present in the dust and a part of this calcium is re-precipitated as calcium carbonate (and even calcium hydrogen carbonate) during the evaporation step. Thus this calcium carbonate is not the "native" calcite in the dust. This is this carbonate which could be dissolved rapidly in the seawater.*

In order to be clearer on this point, we mention in 3.6. the effect of cloud processing: " The material collected in the traps contained 2.6% of Fe and 4.8% of Al (Tab. ES4). This is higher than the initial dust composition (2.3% of Fe and 3.3% of Al), due to preferential dissolution of highly soluble calcium carbonate or possibly calcium hydrogen carbonate formed during the simulation of dust processing in clouds (see section 2.1., Desboeufs et al., 2014).

Frank Pavia: 4) I struggle with the arguments in the first paragraph of section 4 (page 7, particularly lines 34-41). What time interval are these waters seeded over? The dust input units given of 10g dust/m2 are not flux units without a time component, so it is difficult to assess whether this is a feasible dust flux compared to the highest dust pulses or mean annual dust fluxes. Because the dust corresponding to the average areal input was added in such a short time period, I think the sentence in lines 37-38 "Hence, the PEACETIME experiments: : :" must be taken out.

Reply: *We have removed the term of "flux" and replaced it by the term of "quantity". As noted by Frank Pavia, the flux implies a notion of time. In practice, during PEACETIME, dust was quickly sprayed over the four dust amended minicosms (successively, each 'rain' lasting ~ 20 mn) in order to be as synoptic as possible. This 20 mn "rain" time is now mentioned in section 2.1. This rather short duration is not unrealistic as this type of large, rapidly settling events have already been observed in the Mediterranean Sea, and are often associated with low rainfall (Loÿe-Pilot & Martin, 1996): as reported by these authors, "very significant amount of dust can be deposited with only few drops or mist", meaning that those events deposited high fluxes within only few minutes. However, what really matters for the experiment is the quantity of dust deposited rather than how fast it was deposited.*

Ref: Loÿe-Pilot, M. D., & Martin, J. M. (1996). Saharan dust input to the western Mediterranean: an eleven years record in Corsica. In The impact of desert dust across the Mediterranean (pp. 191-199). Springer, Dordrecht.

Frank Pavia: 5) The difference in dissolution kinetics between Th/REE and Al is intriguing, and I would like to have seen the authors speculate on what drives it. Are different mineral phases releasing Th/REE than Al?

Reply: *we now mention in section 4.1. that an unexpected result of the PEACETIME experiments is the contrasting dissolution kinetics of Al relative to Th and REE. Th and REE are (at least partly) carried by specific REE and Th rich phases (Marchandise et al., 2014), that may partly account for the decoupling with Al. Alternatively, the fast dissolution of calcium carbonate or calcium hydrogen carbonate formed during the cloud simulation step could account for REE and Th release (see sections 3.6 and 4.3.).*

Frank Pavia: A back of the envelope calculation, 3.6g dust added, 15% of it presumed to be CaCO3 that dissolves, 0.5ppm hydrogenous 232Th in lacustrine carbonates (Lin et al., 1996) and in pedogenic carbonates (Ludwig and Paces, 2002) gives 1160 pmol of 232Th that could be released into the tank from detrital CaCO3 dissolution. Dividing this by the 300L tank volume gives a _[232Th] of _3.9pM – very close to the 3-5 pM initial rapid increase in 232Th observed at both ION and FAST. This calculation should be done by the authors for REE as well. If this is the case, then Th dissolution in dust may be highly dependent on the detrital carbonate content – which would be a really interesting result. Regardless, it is important to explicitly note that Th and REE release from dust is clearly controlled by multiple phases – a fast dissolving one and a slow-dissolving one – and that this is different from Fe and Al release.

Reply: *We have included the calculation suggested by Frank Pavia, but we have used references concerning carbonates from the Sahara:*
Alternatively, the dissolution of the carbonates from the dusts can release significant amounts of ^{232}Th. For example, the ^{232}Th content of travertine and pedogenic carbonates found in the Western Sahara ranges from 0.5 to 12 ppm (Szabo et al., 1995, Candy et al., 2004, Weisrock et al., 2008). Taking 2 ppm as mean value and considering that carbonate dissolution represents 4.5 % of the dust mass (see section 3.6), it corresponds to a release of 1400 pmol in 300L of seawater potentially yielding an increase of 5 pM, in gross agreement with observations (Fig. 3). While pedogenic calcretes contain sufficient amounts of ^{232}Th and REE to account for the changes of Th and REE concentrations observed during the Peacetime experiments (Prudencio et al., 2011), the ^{230}Th /^{232}Th ratio of these carbonates is generally low (^{230}Th /^{232}Th = 2-5×10-6, Candy et al., 2004), so that it cannot account for the higher ^{230}Th /^{232}Th ratio (~ 8×10-6) of the Th released during the PEACETIME experiments (Fig. 6).

Candy, I., Black, S., & Sellwood, B. W.: Quantifying time scales of pedogenic calcrete formation using U-series disequilibria. Sedimentary Geology, 170(3-4), 177-187, 2004.

Szabo, B. J., Haynes Jr, C. V., & Maxwell, T. A.: Ages of Quaternary pluvial episodes determined by uranium-series and radiocarbon dating of lacustrine deposits of Eastern Sahara. Palaeogeography palaeoclimatology palaeoecology, 1995.

Prudêncio, M. I., Dias, M. I., Waerenborgh, J. C., Ruiz, F., Trindade, M. J., Abad, M., ... & Gouveia, M. A.: Rare earth and other trace and major elemental distribution in a pedogenic calcrete profile (Slimene, NE Tunisia). Catena, 87, 147-156, 2011.

Weisrock, A., Rousseau, L., Reyss, J. L., Falguères, C., Ghaleb, B., Bahain, J. J., ... & Pozzi, J. P.: Travertines of the Moroccan Sahara northern border: morphological settings, U-series datings and palaeoclimatic indications. Géomorphologie: relief, processus, environnement, (3), 153, 2008.

Frank Pavia: 6) The relative fractional solubility of metals is used in calculations of dissolved metal flux from dust derived from thorium isotopes (Hayes et al., 2018; Pavia et al., 2020).
It would be fantastic to calculate the release ratios of Fe, Al, and REE to Th (along with their uncertainties) and provide these in addition to Table 1. These would be an excellent addition to the aerosol-based solubility estimates currently used, though it would also be important to note that using these relative solubilities in Th-based Fe flux estimates could be biased if the differences in metal release kinetics between Fe and Th release are sufficiently large to decouple the release depths of Fe and Th as fine lithogenic particles aggregate and sink from surface waters.

Reply: *The release ratios of Fe, Al, and REE to Th (along with their uncertainties) are now given in Table ES5 and discussed in section 4.4.*

Frank Pavia: 7) There is a mismatch by a factor of 10 between the units on y-axis of Figure 6 and those cited in the text in section 4.3.

Reply: *The factor 10 is now corrected*

Frank Pavia: 8) The points regarding differences in solubility estimates of Th between previous results and this study made in 4.4. are very important. Th solubility is one of the largest sources of uncertainty in Th-based dust flux estimates (Pavia et al., 2020), and different methods give different results. However, authors' points about lateral 232Th inputs are not justified by the data presented in this paper. The solubility of 232Th does not alter the removal residence time of Th in the upper water column. The 230Th-based removal residence times in the upper 250m of the South Pacific Gyre (depths over which Th-based dust flux estimates are integrated) are 1-2 years (Pavia et al., 2020).
Note that the South Pacific Gyre is highly oligotrophic, similar to the Mediterranean – so 1-2 years is likely on the longer end of Th residence times for the upper 250m in the ocean. The diffusive lengthscale for lateral diffusion of Th in the upper water column, given by _x=p (2K_H _t) (Roy-Barman, 2009), for a residence time of 2 years and a lateral eddy diffusivity of 10ˆ3 m2/s, is 355km. So, regardless of the 232Th solubility, lateral lithogenic inputs from the continents should not affect 232Th distributions in the open ocean beyond this distance. Indeed, the lack of lateral inputs affecting the deep Mediterranean, with longer transport timescales from boundary lithogenic sources than in the upper water column in the open ocean, is noted in the conclusion. More work is needed to determine the role of vertical and lateral exchange on 230Th and 232Th budgets, but the conclusions of this study do not justify the conclusiveness of the statements regarding lateral Th fluxes (e.g. "cannot be done", page 12 line 33; "strongly biased by advective inputs" page 12 lines 31-32). These statements should be tempered accordingly. Similarly, the statement on page 13 lines 13-15 should be

adjusted or removed, as the current study does not provide any insights on the importance of advection as a source of 232Th to the open ocean.

Reply: *The sentences raising possibilities of bias in the estimation of Fe and Th solubilities based on the 230Th-232Th method have been tempered or removed. However, we note that the equation relating the time and length during eddy diffusion must be used with care for 2 reasons:*

- It neglects advection. For example, this equation does not account for the Fukushima radionuclide transport across the North Pacific in 2 years (Buesseler et al., 2016).

- the net effect of diffusion depends on both K_h *and the concentration gradient.*

$F = - K_h \, d^{232}Th/dz$

When large gradients occur (coastal ocean/open ocean), it may take more than one diffusion length to totally remove/dilute the high coastal concentrations and reach constant concentration in the open ocean. This is why we add in section 4.4 that "Hence, deducing dust inputs from the $^{230}Th/^{232}Th$ *ratio of surface waters (Hsieh et al., 2012) requires first to consider ocean areas where the water residence time relative to circulation significantly exceeds the Th residence time relative to scavenging (e.g.: part of the south Pacific gyre where the horizontal dissolved* ^{232}Th *gradient tend to vanish (Pavia et al., 2020))."*

Buesseler, K., Dai, M., Aoyama, M., Benitez-Nelson, C., Charmasson, S., Higley, K., ... & Smith, J. N. (2017). Fukushima Daiichi–derived radionuclides in the ocean: transport, fate, and impacts. Annual review of marine science, 9, 173-203.