

Interactive comment on “A mosaic of phytoplankton responses across Patagonia, the SE Pacific and SW Atlantic Ocean to ash deposition and trace metal release from the Calbuco 2015 volcanic eruption” by Maximiliano J. Vergara-Jara et al.

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Q. Questions/comments R. Responses

Q. It contains many vague statements that are not backed up by a careful analysis of the data. For example, the authors conclude that Fe(II) release decreases from dry ash samples over time ('aged ash') and emphasise that it is a key result of their study. However, this trend is not apparent from the dataset presented; Figure 7 shows that

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several measurements corresponding to different ash “ages” produce the same Fe(II) release. A more careful and quantitative analysis is required.

R. For the Fe(II) concentrations, because of the parametric fit to these data to ash loading and the fact they weren't collected specifically to test aging (we noticed afterwards there may have been some decline) with replicates of the exact same loading, it is difficult to show if there is a trend, especially since we agree that there is no clear change between the first two time points. This being the case we have removed comments concerning the potential decline from the manuscript.

Q. The study also includes measurements of other ash (Etna and Chaiten) and dust (Saharan dust, glacial flour, iceberg-borne particles) materials. The reason for selecting these samples is obscure if not random. The data acquired in relation to these samples are almost not used in the discussion.

R. We simply wanted to test if other particles also released Fe(II) upon addition to seawater as there is sparse literature specifically testing this and so tested a broad range of particles from well characterized materials we have in our collection. However, as these are all aged, we agree the comparison is not particularly useful so have removed these parts of the manuscript.

Q. The fresh and brackish water leaching experiments were carried out using two ash size fractions (< 63 μ m and 250-1000 μ m). What does justify the choice of the two size fractions, except perhaps the availability of sieves in the laboratory? How well these size fractions represent the actual ash deposits? What is the corresponding specific surface area of the ash particles in each size fraction? The leaching protocols differ between the different measured parameters. This does not allow the rigorous testing of potential relationships between different ash properties.

R. We have included a new table that summarize all the leaching experiments done in this research, the analysis, the water used for the leachates, etc. In order to better explain the different methods used. The leaching protocols had to differ to make

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some measurements e.g. measurements of major ions in saline waters would not be possible due to the high background level of most ions, measurement of Fe(II) is not meaningfully possible at room temperature etc.

The size fractions used were selected to test the effect from different particle size. The corresponding size fractions used and their respective percentages from the total of the sample are: > 2360 μm (4.54%); < 2360 μm & >1000 μm (6.85%); <1000 μm & >250 μm (31.12%); <250 μm & >125 μm (24.14%); <125 μm & >63 μm (18.04); <63 μm (15.31%). This information is now also included (new lines 215-217).

The main constraint on the selection of ash size fractions was the total mass of unhydrated ash available for experimentation, which generally is very limited for any given study and in our case precludes the robust testing of all possible experimental treatments. We therefore focused on the most meaningful treatments: major ions and macronutrients are effectively undetectable in given background levels in brackish or seawater matrices, and Fe is probably not a significant factor in terms of biogeochemical effects in freshwater systems. Particle size distributions generally vary considerably over the extent of ash plumes (and to some extent over short time scales), hence there is no standard “actual ash deposits” but a range, which for this event has not been to our knowledge characterized. The size fractions reported here are standard sieve sizes, their relation to previous studies is discussed above and they were selected as fractions which could be sieved and still produce enough material to work with (larger, or smaller, sieves would have not yielded enough material to conduct the work described herein from our bulk ash sample). Although the surface area was not estimated, based on previous studies (Brantley et al 1999 and Gauttier et al 2001, op cit. Jones and Gislason 2008), specific surface area will approximately double for each increment in smaller grain size (again based on standard 500, 250, 125, 63 μm series). Ultimately, based on the size fractions represented above, we tested both the dominant size fraction by mass (250-1000 μm) and by surface area (<63 μm), the latter proving an overwhelming contribution to leaching products as demonstrated here.

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Q. Overall, the ms suffers in places from gloss simplifications and insufficient use of the huge literature body existing on the processes controlling the solubility of Fe in airborne mineral particles. The discussion is wobbly and the authors jump to conclusions quickly, although the data do not clearly support them.

R. We have carried out extensive modifications to remediate the gloss simplifications and insufficient use of the huge literature body, following the suggestions from all reviewers particularly removing the material which speculated a decline in Fe(II) release with aging. We focus on the novel aspects, which as commented by other reviewers, concern the Fe(II) release which has been poorly investigated into seawater.

Q. Section 4.1 “Local drivers of 2015 bloom dynamics in Reloncaví Fjord” is a list of the potential factors that could explain the observed bloom and this section could have been written up without any prior data. I do not think it adds any new knowledge that would contribute to improve our understanding of the potential impact of ash inputs to (marine) water bodies.

R. Section 4.1 is a section that was written thanks to the extensive and exhaustive environmental data gathered in this environment. To our knowledge similar biochemical in situ monitoring datasets are not present in the literature that have fortuitously measured, with high time resolutions (h), the potential effect of a volcanic eruption within an environment of similar characteristics like the Reloncaví fjord. We believe that having the possibility to measure the in situ data of a natural water body should be of interest for different scientific disciplines. We acknowledge that there does not appear to have been dramatic changes in the fjord and thus our summary of the shifts observed- which appear to be largely seasonal and not specifically in response to the ash deposition- is not particularly exciting, but this can only be concluded having seen the data.

Q. Attributing Fe release from ash exclusively to the presence of iron-bearing salts is misleading. Leaching and dissolution of the aluminosilicate glass and minerals contained in ash is also a source of Fe(II) and Fe(III) (see Maters et al., 2017; 2017 and

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other studies).

R. We have studied the literature concerning the evidence for iron-bearing salts and agree the evidence for this, whilst multi-faceted, is not entirely conclusive. However, our main line of argument, which was not developed previously, is the temporal development of Fe(II) during the leach experiments. This does show a pulse of Fe(II) released in the first minute of dissolution followed by a closer to steady-state situation later.

The studies quoted demonstrate leaching of Fe(II) at low pH. This is not comparable to work conducted in seawater, because the fraction of dFe leached as Fe(II) is sensitive to the solution pH and shows a non-linear relationship with pH (the ferrozine method used to quantify Fe(II) in the above studies is also prone to artefacts under low pH conditions). Similarly, the stability of Fe(II) in solution is highly dependent on pH. Experiments demonstrating that Fe(II) is leached under acidic conditions cannot therefore be used to extrapolate to seawater either from a concentration, or from a mechanistic perspective.

There are numerous papers providing varying lines of evidence for the release of Fe-bearing salts dominating dFe release over short (minutes) time periods. We accept however that these are not conclusive that this is the only source of dFe (or specifically Fe(II)). Following comments from another reviewer, we also now display the Fe(II) data from ash release as a time series (after ash addition to seawater). The temporal trend suggests that much of the Fe(II) is released in the first minute following addition to seawater suggesting that the origin of this Fe(II) is a highly soluble phase. We have amended the section accordingly (new lines 562-574).

Q. Line 39: should be cloud not plume. Same applies throughout the ms R. Line 39: We refer to plume, because is from the eruption itself, while an ash cloud could form afterward from resuspension of old ash deposits. The ash studied here came from the eruption plume. Ash cloud is used in the context of the satellite analyses.

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Q. Line 48: F not FI but F. Same applies throughout the ms and tables R. Line 48: Correction accepted. Changed all throughout the ms.

Q. Line: 50 "higher than usual" by how much? Two times? An order of magnitude? Outside the multiannual variability? R. Line 50: About two times and up to four times higher (Gonzalez et al 2010; Montero et al., 2011) for corresponding season, Autumn).

Q. Line 52: You should be transparent in the abstract that this is highly speculative (since no other measures in the fjord point to a phytoplankton response to ash addition). R. Line 52: We change the phrase to: Within Reloncaví Fjord, average integrated peak diatom abundances were higher than usual by up to two times (May diatom abundance cell*109 m⁻²), integrated to 15 m depth), with the bloom intensity perhaps moderated due to high ash loadings in the weeks following eruption.

Q. Line 62: How can a micromolar concentration of Fe(II) be released when above you say only nanomolar concentrations of Fe are released? R. Line 62: Note the units are different "nmol l⁻¹" refers to the Fe concentration in solution. "μmol g⁻¹" refers to the Fe in solution per unit of ash. The units/values are correct as stated.

Q. Line 64: This is not justified. First, you assume only Fe(II) is bioaccessible, and second, it is based on Fe(II) decreasing in aged ash which is not well supported by the data. R. Line 64: This is based on the observation that Fe(II) was released, not on how it aged. A room temperature leach with subsequent measurement of dFe would not detect this Fe(II), it would already have re-oxidised and precipitated as Fe(III) before it could even be filtered and preserved. We are not assuming Fe(II) is bioaccessible, or that only Fe(II) is bioaccessible. Irrespective of whether Fe(II) is bioaccessible or not, increasing its concentration increases the bioavailable pool of Fe by maintaining a higher concentration of Fe in the dissolved phase which can be (and is) actively cycled via Fe(III) phases.

Q. Line 67: Meaning. . . R. Line 67: We just wanted to frame this in an environmental context, this is a high fraction relative to what you can observe in the natural environ-

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ment (much higher, for example, than the ratio in bulk seawater and comparable to that observed in a highly-photochemically affected context).

Q. Line 77: 2010 not 2013 R. Line 77: change done, 2010.

Q. Line 81: Why 'therefore'? The preceding sentence deals with a case that is not in a HNLC area of the ocean. R. Line 81: Sentence changed to another connector.

Q. Line 94: Perhaps in fresh water but I imagine any shift in seawater pH is extremely transient and localised due to strong buffering! R. Line 94. Yes, clarified, although the fjord surface layer is relatively fresh and thus more weakly buffered.

Q. Line 99: 2010 not 2013. R. Line 99: change done.

Q. Line 148: Had the ash been rained on in the interval between the eruption and sampling? R. Line 148: No, the ash was gathered from fresh deposition at the eruption nearby area, from ash than had been falling down on the day before.

Q. Line 151: But South Atlantic seawater is presumably not HNLC water, so its properties might lead to findings here only relevant to ash input to the South Atlantic. For example, HNLC seawater might have different types/abundances of Fe-binding ligands. R. Line 151: Yes, in short, the exact seawater used will have several influences on the Fe leached from ash int solution. Ligand concentration being one of them. This affects any leach experiment and is not specific to the work herein. S Atlantic water with a relatively typical dFe starting concentration was used as the most representative seawater supply we could access.

Q. Line 152: Is there a basis for this range? Does it mimic the Calbuco ash loading to the SW Atlantic and SE Pacific regions studied? R. Line 152: As we don't have data about the natural ash loading at the ocean regions studied here after the Calbuco eruption, we can't answer this question. The ash loadings are designed to be broadly comparable to the range used in prior work. There is no clear reason to choose a specific loading, as the loading gradient in any eruption is always very broad both

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spatially and temporally.

Q. Line 167: Again, if South Atlantic seawater is not Fe-limited, then presumably measurements of Fe(II) concentrations in this water cannot be generalised to reflect Fe release behaviour from ash in Fe-limited seawater. For instance, different types/abundances of Fe-binding ligands in HLNC water might strongly influence dissolved Fe concentrations on ash input to seawater. R. Line 167: It's not clear what the reviewer means here, there is no such thing as Fe-limited seawater, Fe-limited refers to phytoplankton status. The ratio of dFe:macronutrients could be used to indicate if seawater is deficient. Generally higher ambient dFe concentrations (i.e. non-dFe-deficient conditions) would lead to saturation more easily, so the Fe-leached from ash would be potentially reduced compared to starting with lower ambient dFe concentrations. With respect to ligands, 'Fe-binding ligands' almost invariably refers to Fe(III)-binding ligands⁵, the effect of which would not be direct on short-term (seconds-1 minute) Fe(II) release into solution. Fe(II)-binding ligands may exist in an environmental context, but they are not thought to compose such a large influence on Fe(II) speciation as Fe(II) is a transient specie the distribution and concentration of which is dominated by redox dynamics rather than by ligand properties.

Q. Line 168: Why is the ash loading concentration different than that used for the trace metals above? R. Line 168: because these are two different experiments. For Fe(II), we noticed that there was pronounced sensitivity to the ash loading, so expanded the range of conditions to see what the very high/low loading/Fe(II) release looked like.

Q. Line 175: What 'dissolution experiments'? Do you mean ash leaching in seawater? R. Line 175: Yes.

Q. Line 179: Should be desert and please specify which, for consistency with specifying the ash source (Etna, Chaiten). R. Line 179: No longer present in manuscript.

Q. Line 180: Please specify sources R. Line 180: No longer present in manuscript.

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Q. Line 183: Please revise heading - species responsible for alkalinity, ions, and nutrients are not mutually exclusive. R. Line 183: heading of point 2.3 changed to: 2.3 Ash samples – DI and brackish leaching experiments.

Q. Line 184: I thought it was Reloncavi Fjord? R. Line 184: This was the fieldsite. But consider that this fieldsite had experienced a huge deposition of ash, we suspected that collecting water which already had experienced a large ash exposure (and at the time of our ash collection still had a visibly high ash loading) would not be particularly insightful for leach experiments. We therefore collected water from an adjacent fjord to conduct our leaching experiments with.

Q. Line 187: Do you mean deionized water here? If so, please say this instead to avoid misinterpretation to mean environmental/fjord fresh water. R. Line 187: Suggestion accepted, now says DI water.

Q. Line 188: 0.18 g ash in 40 mL is 4.5 g/L or a 1:222 ash:water ratio. Where does this come from (it is not from Witham et al. 2005)? R. Line 188: The total amount of that sample was divided in order to have a good number of replicates. Following most of Witham et al., (2005) recommendations, point 5: 1; 2; 3; 4; 8 and 9. Note that although the total mass of unhydrated ash was limited, the ash/water ratio for DI leaching experiments was of the same order of magnitude as for Jones and Gislason 2008, considering the total flow through their reactor. Finally, it's the time scales that are probably most relevant, together with the selection of the finest size fraction.

Q. Line 200: Were saturation indices calculated for all species in solution? R. Line 200: We ran Visual MINTEQ 3.1 for average the ionic composition of the 63 um size fraction (which had the highest yield of leachates) together with three scenarios of pH (5, 6 and 7) and Fe (4.5) – note that since these parameters were not measured for the freshwater experiments they are merely parameterized here based on plausible values (e.g. Fe should be within an order of magnitude of marine leaching following the results shown in Jones and Gislason 2008). The results are included in the Supplementary

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material, and show highly undersaturated conditions for almost all potential minerals except for iron hydroxide species.

Q. Line 222: This should come after “at 3 depths”. R. Line 222: Suggestion accepted.

Q. Line 328: Isn't it 4.5 g/L (0.18 g in 40 ml)? R. Line 328: Suggestion accepted.

Q. Line 335: This is probably just a surface area effect (i.e. smaller size particles for the same mass of ash release correspondingly more ions due to the greater surface area in contact with solution). Leaching not dissolution. R. Line 335: Suggestion accepted.

Q. Line 338: Because CaSO₄ salts are not as soluble? R. Line 338: CaSO₄ salts are secondary minerals, among an array of species that are, according to the charge balance and the results from various time steps, far from equilibrium.

Q. Lines 350-352: I don't see support for this statement. From Figure 7 (right) showing all replicates, the couple of high Fe release values per unit ash mass seem like outliers. In fact two of the lowest ash loadings exhibit among the lowest Fe release per unit mass. R. Lines 350-352: Following comments from another reviewer, we have better grouped the behavior of the metals considering the quality of the fit over the applied ash gradient, and the magnitude of the change in concentration compared to the initial concentrations. New lines 379-388 are therefore re-written, and p values are added to new Figure 6.

Q. Line 356: Be careful with these statements, there is a lot of overlap of error bars so any apparent increase may not be significant. R. Line 356: Suggestion accepted. We have added regression fits and p values to the plots showing changes in trace metal concentration with time. We also discuss which elements we cannot discuss meaningfully due to the limited change compared to background concentrations. We have modified this discussion to exclude elements where we cannot meaningfully determine trends (new lines 379-388).

Q. Line 370: Why this temperature and not room temperature, like the others? R. Line

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370: Fe(II) is unstable at room temperature under oxic conditions (now explained in the text).

Q. Line 374: If not in the legend, at least here in the caption you should state what they are (desert dust, glacial flour, iceberg particles) etc. R. Line 374: No longer in manuscript following earlier comments.

Q. Lines 374 - 375: It seems that the two other volcanic ash (Etna, Chaiten) are included here to represent older ash samples, but if that's indeed the purpose, this is not a valid comparison because the different Fe chemistries (total Fe content, Fe redox speciation, and Fe mineralogy) in these samples are likely to be greater drivers of their Fe(II) release behaviours than the different ash ages. This must be acknowledged, or else I suggest removing the Etna and Chaiten ash from this study altogether. R. Lines 374 - 375: No longer in manuscript following earlier comments.

Q. Line 381: The Figure 7 y-axis reports Fe(II) release in nmol/g. Please be consistent for clarity. R. Line 381: We have shown the Fe(II) results as nmol g⁻¹ in figure 7 because of the sharp curve that results, in Figure 6 we plot the concentration as nM because the propagated error on nmol g⁻¹ becomes huge for those elements that do not show a pronounced change. As the data displayed as nmol g⁻¹ was however also requested by another reviewer, we add it in the supplement.

Q. Line 391: Perhaps only at low ash loadings, it's hard to say from the few data points for 9 month old ash. I would not consider this a clear trend at all, and in fact the Fe(II) release from 4 month old ash is often higher than from 2 week old ash at the same ash loading. R. Line 391: No longer in manuscript following earlier comments.

Q. Line 393: This is not at all supported by the data shown in Figure 7 (left), see my comment above. R. Line 393: No longer in manuscript following earlier comments.

Q. Line 397: Are you sure that this corresponds to volcanic ash and not to volcanic sulphate aerosol? R. Line 397: The UV Aerosol Index largely reflects the strongly UV-

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absorbing (dust) aerosols. Sulphates are weakly/non-absorbing aerosols and therefore thought to have a more restricted contribution to the absorption signal. Reference: Torres, O., Tanskanen, A., Veihelmann, B., Ahn, C., Braak, R., Bhartia, P.K., Veefkind, P. and Levelt, P., 2007. Aerosols and surface UV products from Ozone Monitoring Instrument observations: An overview. *Journal of Geophysical Research: Atmospheres*, 112(D24).

Q. Line 511: Again, have you tested for saturation of Fe(II) (and other species) in your leachates? It would be useful to explore the possibility of secondary phase precipitation explaining decreasing dissolved Fe(II) with increasing ash loading. R. Line 511: (Saturation is tested for in the Supplement). Specifically for Fe(II), Fe(II) is inherently unstable under these conditions, decaying on a timescale of minutes even with the reduced temperature. It therefore doesn't really make sense to us to consider the extent to which Fe(II) is saturated in solution. With respect to dFe, these concentrations are likely over-saturated as ligand concentrations in this same S Atlantic water have previously been determined to be about 1.5 nM.

Q. Line 512: Again, I don't see clear evidence for this statement in the data (e.g., Figure 7 right). R. Line 512: Please see comment above for line 393. We have re-written this section.

Q. Line 520: Although this notion is propagated in the literature, there remains a paucity of evidence for Fe salts on ash surfaces! This section is missing important information on the forms of Fe (Fe(II) and Fe(III) in ash) - in aluminosilicate glass and mineral network and Fe(-Ti) oxide minerals. Will mislead readers to claim Fe salts are responsible again when we know that's not the case. R. Line 520: As per above comment. Our Fe(II) vs time plots show relatively unambiguously that there was a sudden pulse of Fe(II) release into solution occurring between 0-60 s after ash addition. We do not think that the shape of the Fe(II) vs time plot is not consistent with leaching from a solid aluminosilicate glass phase and suspect it is more consistent with a sudden dissolution effect. However we recognize this is not unambiguous and accordingly have rewritten

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(new lines 562-574)

Q. Lines 522 – 524: No. Fast release of Fe(II) is more likely to originate from leaching of the aluminosilicate glass. Please do your homework (e.g., see Maters et al. 2016 and 2017 - those studies done at pH 1, 2 and 5 but are still relevant sources of info on the forms of Fe in ash and its release into solution)! R. Lines 522 – 524: These leaches in acid cannot be extrapolated to seawater at pH 8 (see earlier comment). If it were the case that Fe(II) were released from a mineral phase, we do not think that this would produce the Fe(II) vs time distribution that we observed during the Fe(II) incubation experiments.

Q. Line 525: See earlier comments, this statement is simply not well supported by the available data. R. Line 525: No longer in the text following earlier comments.

Q. Line 527: There's no such thing as acidic surface coatings. The presence of any salts on ash surfaces is the end product of prior reaction between acids (H₂SO₄, HCl) and the aluminosilicate → neutralization. R. Line 527: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 529: How would an acid-base reaction be responsible for Fe(II) conversion to Fe(III)? Presumably the Fe(II) at the ash surface has somehow been oxidised to Fe(III) during storage, or else made to be less mobile in some other way... R. Line 529: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 530: Again, based on the fact that your data do not support the conclusion that aged ash releases less Fe(II), this statement should be removed. In any case, the term 'aged' in the mineral dust/glacial flour/volcanic ash community often refers to material that has interacted with other species during atmospheric transport ('aging'), if anything increasing Fe solubility and Fe(II) mobilisation over time (e.g., see Maters et al. 2016). R. Line 530: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

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Q. Line 532: This is true simply because we know that airborne material (dust, flour, ash) undergoes atmospheric processing, including exposure to inorganic and organic acids and cloud condensation and evaporation cycles, that is likely to modify the Fe solubility and speciation in the material before deposition to water bodies. Please acknowledge the huge body of literature in this area. R. Line 532: we believe that in this statement the reviewer is referring to airborne material that has undergo atmospheric processing due to long transport time-distance. Here we worked with fresh ash that was deposited in the nearby volcano area shortly after its release, thus we are not concerned with processes occurring in the atmosphere days to months after an eruption. We were referring specifically to a method artefact – when conducting a dFe leach at room temperature, any Fe(II) released (or at least a substantial fraction of it) will precipitate before it can be measured as dFe using standard leaching techniques.

Q. Lines 536 – 544: All this should be removed because it surrounds a claim about aging/Fe(II) release that is not supported by the data here. R. Lines 534 – 544: No longer in the manuscript following earlier comments about the temporal development of Fe(II)

Q. Line 552: What aerosols? Please specify since the Fe chemistry in different particulate materials can vary drastically. R. Line 552: The chemistry of these aerosols was highly variable as it refers to a transect over a large area of the offshore Pacific (we clarify the wording in the text “from aerosols collected across zonal transects of the Pacific Ocean”

Q. Line 553: Specify Calbuco 2015 ash. Saying 'fresh volcanic ash' is a gross generalization and completely neglects existing studies reporting variable Fe release from ash, including Fe(II) and Fe(III) release by ash from different eruptions - Maters et al. 2017. Okay that study done at low pH but it shows that Fe chemistry in ash is highly variable and likely plays an important role in Fe release from ash in solution. R. Line 553: Changed to 'Calbuco' as suggested.

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Q. Line 561: Please specify ash or particle, if that's indeed what the satellite detected. The term 'aerosol' in the volcanology context most often refers to sulphate aerosol. R. line 561: For clarity we have replaced 'atmospheric aerosol loading' with 'UV aerosol index'

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