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Discussions

Interactive comment on "Characterisation of aerosol provenance from the fractional solubility of Fe (Al, Ti, Mn, Co, Ni, Cu, Zn, Cd and Pb) in North Atlantic aerosols (GEOTRACES cruises GA01 and GA03) using a two stage leach" *by* Rachel U. Shelley et al.

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General comments:

This paper reports Fe, Al and trace metals composition and solubility in aerosols particles collected in North Atlantic Ocean. Even if it exists a lot of data on the solubility of Fe and major trace metals in Atlantic area (for ex. Clivar, AMT.. campaigns), new data and in particular new perspective for using this data is always interesting. In this idea, the title of this manuscript was promising but finally, it is rather disappointing after reading. Indeed, even if the title implies a discussion on the relation between solubility and aerosol origin, the paper is limited to a dataset of solubility values as a function of air mass back-trajectories. It's very frustrating because the material is present to make this study original and significant. Another purpose of paper is the investigation to different leaching protocol for solubility measurement standardization. This twofold topic (provenance and protocol) makes abstruse the main objective of the paper.

Although this experimental work has been carefully conducted and contains interesting results, it is short of new findings in this current state due to a lack of guidance in the discussion on the results and of comparison with the literature. Consequently, I strongly encourage the authors to work again on this manuscript because your data could bring appreciable and consistent results for the community.

The major highlights proposed in this paper are "trace elements from aerosols from 1) North Africa were always the least soluble, and the most homogeneous . . ., 2) aerosols from the most remote locations were generally the most soluble, but had the most spread in the values of fractional solubility and 3) primarily pollution-derived TEs (Ni, Cu, Zn, Cd and Pb) were significantly enriched above crustal values in aerosols, even in samples of North African origin."

The critical point on this paper is the signification of term "provenance". In the manuscript, the aerosol provenance is considered as the "back-trajectory". Firstly, the back-trajectories were made for an arrival height of 500m, whereas the maximum altitude of boundary layer is often between 200 and 600 m in North Atlantic (Petenko et al., 1996; Fuhlbrügge et al., 2013), and aerosol sampling was in the boundary layer, so it is not automatically consistent. Moreover, the "loading" in various aerosols is not only dependent on the trajectory but also on emissions along the transport of air masses. A same air masses can be a mix between various types of aerosols. In consequent, as solubility is dependent on kind of particles, it's obvious to observe a largest variability of solubility for aerosols from most remote locations in comparison to dust samples (findings 1) and 2)). In one case, it's a same source and in the other case that includes various sources and hence kind of particles. The relevant conclusion of this work should precisely be that aerosol provenance is not sufficient to estimate composition and solubility of trace metals.

From your database and the previous conclusions of Shelley et al. (2015) on the identification of sources of TEs (not provenance) in aerosols, further investigations could enable to emphasize a relationship between TEs solubility and origin. In this purpose, the origin of aerosol is a huge question which demands a more extensive bibliography to provide convincing proof of metals sources. A part of this comparison with bibliography is provided in the session 3.1 and 3.2. Nonetheless, the structuration of the paper is to much confuse to extract the pertinent information (see specific comments). These sessions should only include a summary of appropriate results from Shelley et al. (2015) for the discussion on the link with solubility. Moreover, a relevant bibliography is often missing in the manuscript. Several field campaigns during the last decade (AMMA, DODO, DABEX or SAMUM) + specific works (e.g. Trapp et al., 2010) permitted to improve our knowledge about the African dust composition before and after transport. Even if this literature is focused on major metals as Al, Fe or Ti, this literature about Saharan dust characterisation should be used to validate/discuss your aerosol origin. Moreover, the category "high latitude dust" is very extended with Al/Fe ratio ranging from 0.1 to 1 (L322-334), suggesting a variability of aerosol sources in these samples (see specific comments). The conclusion of authors about the mixed volcanic and anthropogenic origins of GA01 samples is supported only by the back-trajectories (not shown) and a comparison with the TEs concentrations in volcanic ash from Achterberg et al. (2013), but no comparison on elemental ratios is provided. Is this variability is consistent with the typical composition of volcanic or cold environment dust? Again, several papers report Fe or metals content in high latitude volcanic regions producing dust as Iceland (e.g. Baratoux et al., 2011, Óladóttir et al., 2008 and 2011). It could be interesting to compare with these data for discriminating the origin of this high latitude dust.

The third conclusion of a paper is that polluted derived TEs were significantly enriched above crustal values in aerosol and notably in dust samples (A1-15), on the basis of comparison with UCC. This conclusion is already in Shelley et al. (2015) for GA03 cruises. The new information could be for GA01 for high latitude dust, but this work is not done. Furthermore, I'm not agree with your conclusion on the enrichment "even in samples of North African origin". As a matter of facts, Shelley et al. (2015) conclude that except Cd, the "pollution-derived" elements present EFs less than 10 with respect to Al in the African samples (See Shelley et al., 2015, figure 6). Moreover, your main argument is that these elements have some significant increase from the UCC mass ratio in your dust samples (see specific comments: P11,L336). However, it's known that the production of mineral dust is associated to a chemical fractioning due to the size partitioning between coarse rich-Si grains and the finest clay fraction during sandblasting. It means an enrichment in Al, Fe, Ca.. in dust particles in comparison to soil (Lafon et al., 2006). Thus, the authors are surprised at Al/Fe ratio around 0.76 (P9, L275). Yet, this value is fully consistent with the common knowledge on African dust (see previous comment on bibliography + e.g. Formenti et al., 2011 or 2014 and ref therein or Lazaro et al., 2008). Due to the trace metals partitioning in soil size fraction, this fractioning and hence enrichment probably happens also for trace metals in mineral dust. Your data seem to confirm this trend, previously observed by Trapp et al. (2010) after long-range transport. it's bad that this point of view is not addressed here. . .

Finally, a part of the manuscript is focused on the standardization of methods to estimate TE solubility. The conclusion on this session is not convincing for me because the proposed "upper limit" is not supported by the "reality" of aerosol dissolution in atmospheric or sea waters. The 25% acetic acid leaching protocol includes a heating at 90°C during 10 min. This leaching protocol is issued from Berger et al. (2008) who recommend the heating to dissolve the refractory forms of metals bound with intracellular protein or intracellular trace metals in particles collected in river plumes, i.e. organic macromolecules bound trace metals (heating enabling the degradation of these polymeric structures). Your arguments are based on the capacity of this protocol to reproduce acid digestion in gut krill.. Yet, the dissolution in this condition is probably more aggressive than gut krill due to this step of heating. The risk with this protocol is to access to refractory form which is never available for phytoplankton. Besides in your data, the solubility of Al is higher than the one of Fe with this protocol, isn't it due to leaching some aluminum from the refractory alumino-silicate minerals (see specific comments, P13, L400)? What is the relevance of this refractory forms of TEs for estimating their bioavailability? Do you have literature to support the fact of organo-metal complexs are bioavailable? In my opinion, it could be more interesting to use this 25% acetate soluble fraction as a proxy of organically bound trace metals and discuss on the link between source/instantaneous solubility and chemical form of trace metals, rather as an "upper limit" of solubility which is probably never reach in the natural conditions. . .

Specific comments :

The paper is a part of range of publications associated to Atlantic Geotraces campaigns. The presented data analysis is supported by numerous other works issued from these campaigns. The crucial information to understand the results is not always specified in the text and it's necessary to study the cited papers to understand the interpretation of results. For example, the back-trajectories are at the heart of the discussion in this paper, but they are not available in the text (see below). The categories of trace metals "lithogenic", "anthropogenically enriched" and "mixed source" which are issued from Shelley et al. (2015) appear P9, L336 without previous explanation. . .

Moreover, the structuration of the paper is not linear and implies several repetitions or meandering discussions, which drow up the conclusions. This paper has no clear guidance and is hard to follow. For example: In "Introduction": a first background on the leaching protocol between L67 and 86, then a second part of this background with repetition is presented between L95 and 124. Or In "Results and Discussion", the discussion on the ratio Fe and Al begins L255 up to L265 in session 3.1, then continues in L275, then is addressed in the next session 3.2 (L 295-335). The UHP water soluble

fraction starts to be discussed in the session 3.2., then be continued in the session 3.3. "Aerosol solubility". . . I advise to re-organise your paper, with a session: "metals origin" including a "clear" summary of Shelley et al. (2015) focused on their conclusions about origin of Fe and TEs as a function of provenance completed with a work on identification of sources from adapted bibliography then a second session presenting "solubility" not as a function of backtrajectories but a function of metals source (and in consequence with adapted figures).

Certain experimental points need also to be specified to clarify the conclusions of this work.

- P5, L148, please precise the cut-off diameter (or PM fraction: TSP, PM10..) of the aerosol sampler.

- P7, L226-L228 and session 3.4: The determination of nss-SO42- is calculated from soluble Cl-. However, it's known that there is a potential depletion of Cl- during transport of sea salts due to the reactivity with anthropogenic gas in particular acid gas as HNO3. The probability of this depletion increases with the increase of acidity (e.g. Kerminen et al., 1998; Yao et al., 2003; Newberg et al., 2005; Chi et al., 2015). In consequence, the fraction of nss-sulfate could be overestimated. Moreover, your method of calculation of acidity excluded all the organic acid, such as oxalic acid, formic acid. . .which are observed in marine atmosphere (e.g. Kawamura et al., 2017). Lastly, acidity measurement based exclusively on sulfate and nitrate implies that these species are in their acid forms. However, it's known that these compounds are associated to neutralizing compounds as NH4+ (Weber et al., 2016). In general, ammonium concentrations or Cl-depletion are used to estimate the aerosol acidity (Newberg et al., 2005; Hennigan et al., 2015). You mention all this literature and these works (L512-524) and you propose that "these approaches should be considered for future studies". Only even now, without at least an estimation of neutralised fraction, I think that your method suffers too much uncertainties to provide robust conclusion. So, the session 3.4 on the link between solubility and your "acidity" should be removed or completed with cation measurements.

- P8, L238: The air masses of collected samples in the cruise GA01 are not shown. “High latitude dust” includes both dust from paraglacial regions and volcanic lands. Thus, even if the provenance is “high latitude dust”, the origin could be different. For the longest distance between “high latitude” and R/V, a mixing with other sources could have occurred: the collected filters close to Europe (G1-G6) could be feed by various other sources (North of Europe, Europe, marine..) in comparison to the samples G12 or G14...Please show back-trajectories for at least one of the samples close to Europe and another close to North Atlantic.

- P8, L246: replace 2015 by 2014 in reference: Conway and John. And P20, L627 add 2014 in this reference.

- P8, L258: Even if the correlation between Fe and Al in “high latitude dust” samples (= Geovide samples, please be homogeneous between text and Figure 2) is good, the ratio Fe/Al is variable (Figure 3), suggesting various mineral source: please complete this discussion.

- P8, L260 to P9L265: “no correlation between Fe and Al in the samples of N. American (r2=0.153..) and marine (r2=0.016..) provenance”. However in the figure 2b, the plots between Fe and Al concentrations show a R2= 0.983 for N. American aerosols, and R2=0.758 for Marine aerosol. Why is this difference between text and figures? On the basis of a bad correlation, you argue a strong influence of anthropogenic emissions on the Fe/Al ratio in N. American samples. Yet, the ratio (0.86) is consistent with a mineral origin. The quality of correlation changes all the discussion on the origin of Fe, so please clarify that.

- P9, L273 : You propose that “other sources are responsible for residual variance” for metals as Ni or Cd. It could be useful for the discussion on solubility to distinguish correlation (and consequent residual variance) between TEs and Al for each provenance as for Fe. The figure 3 seems show that all the TEs are correlated with Al in the N.

African samples, meaning probably that the anthropogenic influence is poor in these samples.

- P10, L322: “the most heterogeneous group”, for what?

- P11, L336 : Why do you consider all the metals as anthropogenically enriched whatever the provenance whereas all these metals in dust samples (A1-A15) are probably originated from dust from the enrichment factor calculated in Shelley et al. (2015)?

- P11, L350 : Why do you use a PMF analysis with 2 profiles whereas at least 3 are potentially present in your samples : African dust, Anthropic and High latitude dust ? Did you take only trace metals in PMF anlaysis? Nitrate or nss-Sulfate are good proxies to discriminate anthropogenic source. Moreover, PMF is a stastistical method, even if the factor 2 is richest for “anthropogenic” metals, that doesn’t mean that this factor doesn’t include a mineral fingerprint, for example the high latitude dust. It’s clear for the A1-A15 samples, the high contribution of finger 2 is probably due to the fact that metals from mineral fingerprint is taken into account in this factor. This method with your applied conditions is not sufficiently discriminating to be useful here. The discussion on PMF analysis should be removed, because it provides no appropriate information on the provenance of TEs.

- P12, L382-389: I don’t understand why this paragraph is here? A bad cut and paste?

- P13, L398: Why do you present these data? It’s not new that the solubility decreases with the total Al content (e.g. Baker et al., 1996) and your results don’t provide new conclusion. On the contrary, it could be interested to plot the solubility of TEs (no Fe) as a function of atmospheric loading or Al concentrations. Firstly, that enables to valid or not your assumption on the role of scattering in our data in this trend. Secondly, it could be interested to compare the behaviour of Fe (a proxy of mineral dust) with the ones of anthropogenic trace metals.

- P13, L400: I wonder really if the highest Al solubility in comparison to Fe is not due to the dissolution of refractory alumino-silicate minerals. Ti and Fe have the same behavior between UHP-water and 25% acetic acid dissolution in dust samples (figure 5) and both of them are in part as oxide in mineral dust, i.e. “refractory” even at high temperature. Please complete this discussion.

- P13, L403-410: This paragraph is unclear: the first sentence is too long and confused and what is the link between your data and the Madcow MODEL?

- P13, L411-420: This conclusion is interesting but without link with the results presented in this session.

- P14, L451: The discussion around these results is for me off topic. It is a pity that this paragraph be discussed only in terms of comparison between UHP water and seawater protocol, it would be interesting to discuss precisely in terms of origin of metals and solubility in the two protocols. But again, the assumption, which is that the origin of trace metals is homogeneous and anthropogenic, doesn’t enable to identify a link between solubility and chemical form. For example, could you distinguish by coloring the different origin of metals in the figures 7 (as for Fe) to see if a same metal present different behaviours for solubility?

- Figures 5 and 6: No uncertainty is provided in your graphs for the data, could you add this information?

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