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

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16 General comments:

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

28 **Thank you for your review.**

29 **The discussions about standardisation have been removed.**

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

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

41 **The focus has changed: the main findings are now that (1) there are exceptions to the**
42 **general trend that fractional solubility of TEs is inversely related to atmospheric loading.**
43 **The fractional solubility of Mn, Zn and Cd appears to be independent to atmospheric**
44 **loading, and (2) air mass back trajectories are not sufficiently discriminating to identify**
45 **aerosol source.**

46 The critical point on this paper is the signification of term “provenance”. In the manuscript,
47 the aerosol provenance is considered as the “back-trajectory”. Firstly, the back-trajectories
48 were made for an arrival height of 500m, whereas the maximum altitude of boundary layer

49 is often between 200 and 600 m in North Atlantic (Petenko et al., 1996; Fuhlbrügge et al.,
50 2013), and aerosol sampling was in the boundary layer, so it is not automatically consistent.

51 **The GA01 back trajectories presented in the Supplementary Material of Shelley**
52 **et al. (2017) were simulated for arrival heights of 50, 500 and 1500 m. The back**
53 **trajectories for GA03, presented in Shelley et al. (2015) have been redrawn with**
54 **the same three arrival heights as the GA01 samples (50, 500 and 1500 m), to**
55 **include at least one arrival height in the MBL. The four representative AMBTs**
56 **from GA03 and all AMBTs from GA01 can now be found in the Supplementary**
57 **Material (Fig. S1).**

58

59 Moreover, the “loading” in various aerosols is not only dependent on the trajectory but also
60 on emissions along the transport of air masses. A same air masses can be a mix between
61 various types of aerosols. In consequent, as solubility is dependent on kind of particles, it's
62 obvious to observe a largest variability of solubility for aerosols from most remote
63 locations in comparison to dust samples (findings 1) and 2)). In one case, it's a same source
64 and in the other case that includes various sources and hence kind of particles. The relevant
65 conclusion of this work should precisely be that aerosol provenance is not sufficient to
66 estimate composition and solubility of trace metals.

67 **This is now a key conclusion to the paper. However, the regional groupings, as**
68 **determined by AMBT, are retained as a way of grouping the data to look at regional**
69 **variations in fractional solubility.**

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

94 **Further discussion of the high latitude dust sources is now included in the text, and a**
95 **table of elemental ratios from the various studies in regions that contribute aerosols to**
96 **the North Atlantic is included in the Supplementary Material (Table S2).**

97

98 The third conclusion of a paper is that polluted derived TEs were significantly enriched

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

118 **The original intention was to argue that the UCC ratio is not representative of North African**
119 **dust inputs, but that the ratio we observed is consistent with other studies. We don't think that**
120 **the North African dust is enriched with pollution-derived elements, but that there could be a**
121 **component of aerosols coming from Europe mixed in with the Saharan end-member, which is**
122 **also consistent with other studies (e.g. Baker and Jickells, 2017). A new table has been included**
123 **in the Supplementary Material (Table S1), which includes elemental ratios from studies in the**
124 **AMBT regions. It does not include literature data from a Saharan end-member as this was**
125 **discussed extensively in Shelley et al. (2015).**

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

145 **We absolutely agree that this is an upper limit, and potentially an over-estimation of the upper limit. However, we feel that**
146 **the use of the heating step is justified as we wanted to use exactly the same protocol as the SPM leaches done on GA01, and**
147 **some GA03 samples to allow direct comparison between the two datasets. A key goal of this work was to link the**
148 **atmospheric inputs to processes occurring in the ocean. Data from the aerosol leaches and dissolved and particulate trace**
149 **elements indicate that atmospheric inputs are not the dominant source of Al, Fe or Pb along the GA01 transect (Menzel-**
150 **Barraqueta et al., Tonnard et al., and Zurbrück et al., submitted to this special issue).-However, we have acknowledged**

151 that there could be an overestimation of the upper-limit of solubility in the text (from line 208). We feel that if refractory
152 metal is liberated it has the potential to be bioavailable to some micro-organisms, e.g. Tricho (Rubin et al., 2011). In future, it
153 would be a good idea to conduct experiments to test the difference in fractional solubility estimates using this protocol
154 with/without the heating step on different types of aerosols.

155

156 In answer to your question about the bioavailability of organically-complexed TEs, the review by Shaked and Lis (2012)
157 investigates this question, and provides examples of literature that supports this for Fe. This paper is cited in the
158 manuscript.

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161 Specific comments :

162 The paper is a part of range of publications associated to Atlantic Geotraces campaigns. The
163 presented data analysis is supported by numerous other works issued from these campaigns.
164 The crucial information to understand the results is not always specified in the text and it's
165 necessary to study the cited papers to understand the interpretation of results. For example,
166 the back-trajectories are at the heart of the discussion in this paper, but they are not available
167 in the text (see below). The categories of trace metals "lithogenic", "anthropogenically
168 enriched" and "mixed source" which are issued from Shelley et al. (2015) appear P9, L336
169 without previous explanation. . . **Additional wording has been added to this text that we
170 hope provides suitable clarification. The text starting at Line 454 now reads "Figure 5
171 highlights the distinction between the lithogenic elements, Al, Fe and Ti (universally low
172 solubility in UHP water, mostly < 20 %, and extremely low solubility of North African
173 aerosols, < 1 %), and the anthropogenic, pollution-dominated elements, Ni, Cu, Zn, Cd
174 and Pb (solubility up to 100 %). Manganese (Mn) and Co have both lithogenic and
175 anthropogenic sources, so are classified as "mixed-source", and have intermediate
176 solubilities."**

177 Moreover, the structuration of the paper is not linear and implies several repetitions or
178 meandering discussions, which draw up the conclusions. This paper has no clear guidance
179 and is hard to follow. For example: In "Introduction": a first background on the leaching
180 protocol between L67 and 86, then a second part of this background with repetition is
181 presented between L95 and 124. Or In "Results and Discussion", the discussion on the ratio
182 Fe and Al begins L255 up to L265 in session 3.1, then continues in L275, then is addressed
183 in the next session 3.2 (L 295-335). The UHP water soluble fraction starts to be discussed
184 in the session 3.2., then be continued in the session 3.3. "Aerosol solubility". I advise to re-
185 organise your paper, with a session: "metals origin" including a "clear" summary of Shelley
186 et al. (2015) focused on their conclusions about origin of Fe and TEs as a function of
187 provenance completed with a work on identification of sources from adapted bibliography
188 then a second session presenting "solubility" not as a function of back trajectories but a
189 function of metals source (and in consequence with adapted figures).

190 **The problem with repetition has been addressed through restructuring and rewriting sections.**
191 **There are new sections headings: 3.3.1. Identifying sources of TEs. The 'solubility' section is**
192 **still structured by AMBT category because clear sources could not be identified that would**
193 **have enabled reorganising the data accordingly. However, a new section has been included**
194 **(Section 3.4) at the end of the manuscript that discusses sub-groups within the AMBT**
195 **categories that are suggested by cluster analysis of the total TE data and the fractional**
196 **solubility of TEs.**

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

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

199 aerosol sampler. **TSP has been added to text. Line 138.**

200 P7, L226-L228 and session 3.4: The determination of nss-SO₄²⁻ is calculated from soluble Cl⁻.
201 However, it's known that there is a potential depletion of Cl⁻ during transport of sea salts due to the
202 reactivity with anthropogenic gas in particular acid gas as HNO₃. The probability of this depletion
203 increases with the increase of acidity (e.g. Kerminen et al., 1998; Yao et al., 2003; Newberg et al.,
204 2005; Chi et al., 2015). In consequence, the fraction of nss-sulfate could be overestimated.
205 Moreover, your method of calculation of acidity excluded all the organic acid, such as oxalic acid,
206 formic acid. . . which are observed in marine atmosphere (e.g. Kawamura et al., 2017). Lastly,
207 acidity measurement based exclusively on sulfate and nitrate implies that these species are in their
208 acid forms. However, it's known that these compounds are associated to neutralizing compounds as
209 NH₄⁺ (Weber et al., 2016). In general, ammonium concentrations or Cl⁻-depletion are used to
210 estimate the aerosol acidity (Newberg et al., 2005; Hennigan et al., 2015). You mention all this
211 literature and these works (L512-524) and you propose that “these approaches should be considered
212 for future studies”. Only even now, without at least an estimation of neutralised fraction, I think that
213 your method suffers too much uncertainties to provide robust conclusion. So, the session 3.4 on the
214 link between solubility and your “acidity” should be removed or completed with cation
215 measurements.

216 **As suggested, this section has been removed.**

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

224 **Agreed. All of the AMBTs from GA01 have been reproduced and can be found as Figure S1 in**
225 **the Supplementary Material. The four representative AMBTs from GA03 have been redrawn**
226 **and are also included in Figure S1.**

227

228 P8, L246: replace 2015 by 2014 in reference: Conway and John. And P20, L627 add 2014 in this
229 reference. **Done.**

230 P8, L258: Even if the correlation between Fe and Al in “high latitude dust” samples (= Geovide
231 samples, please be homogeneous between text and Figure 2) is good, the ratio Fe/Al is variable
232 (Figure 3), suggesting various mineral source: please complete this discussion. **This discussion can**
233 **now be found starting at line 345.**

234

235 P8, L260 to P9L265: “no correlation between Fe and Al in the samples of N. American ($r^2=0.153..$)
236 and marine ($r^2=0.016..$) provenance”. However in the figure 2b, the plots between Fe and Al
237 concentrations show a $R^2=0.983$ for N. American aerosols, and $R^2=0.758$ for Marine aerosol. Why
238 is this difference between text and figures? On the basis of a bad correlation, you argue a strong
239 influence of anthropogenic emissions on the Fe/Al ratio in N. American samples. Yet, the ratio
240 (0.86) is consistent with a mineral origin. The quality of correlation changes all the discussion on
241 the origin of Fe, so please clarify that.

242 **This was a mistake and has been corrected, starting at line 285.**

243 P9, L273 : You propose that “other sources are responsible for residual variance” for metals as Ni or
244 Cd. It could be useful for the discussion on solubility to distinguish correlation (and consequent
245 residual variance) between TEs and Al for each provenance as for Fe. The figure 3 seems show
246 that all the TEs are correlated with Al in the N. African samples, meaning probably that the
247 anthropogenic influence is poor in these samples.

248 **This is not done as a new Figure 4 and discussion has been added instead, which includes all TEs under**
249 **discussion.**

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

251 **Of the Fe/Al ratios. This wording has been deleted. It now reads, ‘In contrast, samples from the most**
252 **remote locations, the Marine and High Latitude aerosols, had the most spread in their**
253 **fractional solubility and elemental ratios....’.** Starting at line 604.

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

257 **We don’t, we had previously argued that the samples had a relatively low concentration of Al**
258 **compared to other elements.**

259
260 P11, L350 : Why do you use a PMF analysis with 2 profiles whereas at least 3 are potentially
261 present in your samples : African dust, Anthropogenic and High latitude dust
262 ? Did you take only trace metals in PMF analysis? Nitrate or nss-Sulfate are good proxies to
263 discriminate anthropogenic source. Moreover, PMF is a statistical method, even if the factor 2
264 is richest for “anthropogenic” metals, that doesn’t mean that this factor doesn’t include a
265 mineral fingerprint, for example the high latitude dust. It’s clear for the A1-A15 samples, the
266 high contribution of factor 2 is probably due to the fact that metals from mineral fingerprint
267 is taken into account in this factor. This method with your applied conditions is not
268 sufficiently discriminating to be useful here. The discussion on PMF analysis should be
269 removed, because it provides no appropriate information on the provenance of TEs.

270 **The model is not stable with more than two factors, due to the relatively small dataset. This is**
271 **why only two factors were used. We have tried to remove the North African samples to look for**
272 **other groups of TEs that would be diagnostic of other sources, but a crustal factor is always one**
273 **of the two factors. We also tried this with excess metal (assuming the N. African ratio as the**
274 **reference ratio), but the same thing happened. We also tried adding the NO₃- data to the**
275 **analysis, but with no new information generated.**

276 **We agree that the PMF provides limited evidence for sources other than mineral dust, but**
277 **include this figure (Fig. S2) in the discussion because of its inability to identify sources, and as a**
278 **reason to try another multivariate statistical approach (cluster analysis) which is presented**
279 **later in the manuscript.**

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

281 **This sentence has been reworded, ‘Furthermore, the ability of models to replicate subtleties in**
282 **aerosol TE solubility may prove critical in forecasting ecosystem impacts and responses. Due to**
283 **the magnitude of North African dust inputs to North Atlantic region, this is a particular**
284 **challenge and is compounded by additional unknowns such as how aerosol acidity will be**
285 **impacted by the combined effects of increasing industrialisation/urbanisation, and changes in**
286 **the magnitude of future mineral dust supply and biomass burning (Knippertz et al., 2015;**
287 **Weber et al., 2016).’** Starting at line 553.

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

295 **Figure 4 has been redrawn and replaced using all TEs. The main conclusion is that Mn, Zn and**
296 **Cd do not follow the same trend of having an inverse relationship with atmospheric loading as**

297 **Fe and Al.**

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

303 **This is done starting at line 432. ‘Although, we should not rule out that this effect is the**
304 **result of the heating step in the 25 % acetic acid leach attacking the aluminosilicate**
305 **matrix. Further experimentation with and without the heating step should resolve this**
306 **issue.’**

307

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

310 **This has been moved to a new section (Section 3.5) as we wanted to draw attention to how important it**
311 **is to accurately parameterise fractional solubility. This section also includes a short discussion on**
312 **modelling Fe and Mn.**

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

315 **This conclusion is now supported with evidence from this study and starts at line 570.**

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

323 **Figure 6 – the samples have been colour-coded and a table (Table 1) has been added that shows which**
324 **groups of samples have slopes that do not differ significantly from 1.0. We do not think that the origin**
325 **of the metals are homogeneous (although the North African sample TE composition is more**
326 **homogeneous than for the other groups), for the precise reason that multiple sources contribute to the**
327 **aerosols in each region, as well as mixing occurring en route. Perhaps this is why no obvious**
328 **relationship is seen between the samples being leached with either UHP water or seawater. Also,**
329 **perhaps primarily because of the amount of mixing before collection, so far from sources, we are having**
330 **difficulty identifying sources.**

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

333 **Error bars have not been added because of the problem with determining the SD of the fractional**
334 **solubility. In Figure 5, the addition of error bars makes it impossible to distinguish the different**
335 **symbols.**

336

337

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