

1 **Dissolved Al in the zonal N Atlantic section of the US GEOTRACES 2010/2011**  
2 **cruises and the importance of hydrothermal inputs**

3

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12 **Abstract**

13

14 The distribution of dissolved aluminium determined during GA03, the US  
15 GEOTRACES North Atlantic Transects (US GT NAZT) shows large inputs to the basin  
16 from three main sources, atmospheric deposition, outflow from the Mediterranean,  
17 and inputs from hydrothermal sources along the Mid Atlantic Ridge (MAR).

18 The partial dissolution of atmospheric aerosols emanating from the Sahara  
19 yield high concentrations of dissolved Al in the surface waters of the basin and are  
20 used to estimate the geographical pattern of dust deposition. The Mediterranean  
21 outflow delivers a large source of dissolved Al to the intermediate waters of the  
22 eastern basin and its subsequent distribution within the basin can be explained by  
23 simple isopycnal mixing with surrounding water masses.

24 Hydrothermal venting at the Trans-Atlantic Geotraverse (TAG) hydrothermal  
25 field in the MAR produces a neutrally buoyant plume that introduces copious  
26 quantities of dissolved Al (with concentrations of up to 40nM) to the deeper waters  
27 of the North Atlantic that can be seen advecting to the west of the MAR. The  
28 concentration of dissolved Al in the deep waters of the eastern basin of the Atlantic  
29 can be accounted for by admixing the MAR Al enriched plume water and Antarctic  
30 Bottom Water (AABW) as they pass through the Vema Fracture Zone. The data sets  
31 show no evidence for biological remineralisation of dissolved Al from Si carrier  
32 phases in deep waters.

33

34

35 **Introduction**

36

37

38 Since the development of the first reliable methodology for determining  
39 dissolved Al in natural waters (Hydes and Liss, 1976) and its application to coastal  
40 and then vertical profiles in the Atlantic Ocean, there has been considerable  
41 disagreement within the oceanographic community about the major sources and  
42 sinks of dissolved Al to the oceans. Identifying and quantifying sources, sinks and

43 transfer processes of dissolved Al are fundamental prerequisites to successfully  
44 modelling their distributions and using them as tracers of both contemporary, and  
45 through sedimentary records, historical oceanic processes, one of the main goals of  
46 the GEOTRACES program (GEOTRACES, 2006, Science Plan, Scientific Committee on  
47 Oceanic Research, Available online at [http://www.geotraces.org/science/science-](http://www.geotraces.org/science/science-plan)  
48 [plan](http://www.geotraces.org/science/science-plan)).

49

50 The problem of source and sink identification has been particularly  
51 noteworthy in the case of dissolved Al because as the most abundant metallic  
52 element in the Earth's crust and one of the first reactive trace elements for which  
53 reliable trace analytical methodology became available (Hydes and Liss, 1976), it  
54 received widespread attention from a large number of investigators within the  
55 oceanographic community. It became apparent fairly quickly that Al distributions  
56 showed large and potentially interesting vertical variations within the water column  
57 as well as significant inter- and intra-basin fractionation as seen in the North and  
58 South Atlantic (Hydes, 1979, Orians and Bruland, 1985, 1986, Measures, 1995).

59

60 The relative roles of biotic and geochemical processes on surface Al  
61 distributions have been debated since the first studies of the marine cycle of Al were  
62 undertaken. Hydes (1977), as a result of clay dissolution experiments, first  
63 suggested that sediment dissolution might be responsible for supplying dissolved Al  
64 to the water column and that biological uptake processes in surface waters might be  
65 responsible for depleting Al values below the concentrations that would be expected  
66 from clay solubility. This proposed biological mechanism was later expanded to  
67 explain the co-variation of Si and Al in the Mediterranean, as geochemical cycles of  
68 dissolved Si and Al could be coupled through diatom uptake in surface waters and  
69 remineralisation at depth (Mackenzie et al., 1978). Thus started a debate in the  
70 literature as to whether dissolved Al was under biological or inorganic control.  
71 Caschetto and Wollast (1979a), with seasonal data from the Mediterranean,  
72 reinforced the biological argument and stated that their distributions were  
73 incompatible with precipitation-dissolution mechanisms of clay minerals. Using

74 data from the North Atlantic and Pacific, Hydes (1979) responded by suggesting that  
75 surface water Al concentrations were set by deposition and dissolution of  
76 atmospheric particles and that passive scavenging removal by the siliceous  
77 skeletons of dead organisms whose organic coatings had been degraded was the  
78 likely removal mechanism, i.e. not active biological uptake. Additionally, he pointed  
79 out that in his Atlantic and Pacific profiles the data did not show a correlation with  
80 Si distributions and thus the Mediterranean must be anomalous.

81

82 Pore water results from the Mediterranean and North Sea obtained by  
83 Caschetto and Wollast (1979b) showed high concentrations of dissolved Si and Al  
84 suggesting the sediments could be a deep water source of Al to the water column,  
85 but they disputed that simple equilibrium with clays were the driving mechanism.  
86 Additional deeper water column data from the Mediterranean and new profiles  
87 from the western Atlantic obtained by Stoffyn and Mackenzie (1982) showed that  
88 their earlier Al:Si correlations broke down and in some places showed slopes that  
89 were the reverse of their earlier ones and the idea that remineralisation of Si phases  
90 was responsible for elevated deep water Al concentrations was abandoned. Further  
91 work by Hydes (1983) in the eastern Atlantic again showed no relationship with Si  
92 cycling but reinforced the concept of eolian deposition as a source to surface waters.  
93 This source to surface waters was then supported by additional work by Measures  
94 et al. (1984), Moore and Millward (1984), and Orians and Bruland (1985, 1986),  
95 who also estimated deep water residence times of dissolved Al to be of the order  
96 150 years.

97

98 In a series of lab experiments and in profiles from the high energy New  
99 England shelf, Moran and Moore (1991) showed that resuspension of sediments  
100 played a role in adding dissolved Al to bottom waters. They also showed that  
101 passive scavenging of dissolved Al on dead diatoms was a rapid process and could  
102 be modeled in a manner similar to that of dissolved Th (Moran and Moore, 1992).  
103 The potential for a hydrothermal source of Al to the oceans was first suggested by  
104 Stoffyn and Mackenzie (1982) but was discounted by Hydes et al. (1986) who

105 attributed the deep water maximum in their Mid Atlantic Ridge (MAR) profile at  
106 43°N to sedimentary remobilisation within the axial valley of the MAR, as there was  
107 no complementary Si enrichment.

108

109 Thus, by the early 1990's, the ideas about the sources of Al to the ocean had  
110 settled around atmospheric inputs, sedimentary sources, and abiotic removal by  
111 scavenging onto particles with some potential for biological transport, but not one  
112 exclusively Si based. Since that time the distribution of dissolved Al in the ocean has  
113 been used as a tracer of atmospheric input and its distribution in the deep water has  
114 been interpreted as predominantly arising from the subduction and advection of  
115 water masses with input from resuspended sediments.

116

117 Recently, the biotic influence on Al and Si cycling has been revisited, based on  
118 observed correlations between Si and Al, described by Middag et al. (2009, 2011) in  
119 the Arctic and North Atlantic Ocean. This uptake and release process has been  
120 modeled (van Hulton et al., 2013) using a reversible scavenging model, conceptually  
121 similar to that used to reproduce oceanic Th distributions (Bacon and Anderson,  
122 1982). However, the role of hydrothermal vent processes in adding dissolved Al to  
123 the deep waters of the Atlantic was specifically excluded, invoking only mechanisms  
124 of advection and reversible scavenging by biogenic Si (van Hulton et al., 2013).

125

126 In this manuscript, we present the dissolved Al data from GA03, the US  
127 GEOTRACES 2010 and 2011 cruises that provided quasi-zonal coverage of both the  
128 eastern and western basins of the North Atlantic. The transects show very clearly  
129 the effect of hydrothermal venting at the Trans-Atlantic Geotraverse (TAG) Mid-  
130 Atlantic Ridge (MAR) vent site in providing copious quantities of dissolved Al to the  
131 mid and deep water column of the North Atlantic. They also show that for large  
132 areas of the thermocline waters of the Atlantic Ocean, the distribution of dissolved  
133 Al can be explained simply by mixing a high Al Mediterranean Outflow Water  
134 (MOW) source with a low Al Antarctic Intermediate Water (AAIW) source with no  
135 evidence of Al input to, or removal from, the water column. We will also show that

136 in the eastern North Atlantic, in a region of intense biological activity in surface  
137 waters, there is no evidence of dissolved Al remineralisation in the underlying  
138 intense oxygen minimum ( $\sim 45 \mu\text{M O}_2$ ), nor is there evidence of the surface water  
139 Al:Si signal being imprinted on the deep waters through the remobilisation  
140 processes as has been proposed elsewhere (Middag et al., 2009, 2011; Van Hulton et  
141 al., 2013).

142

143

## 144 **2. Methods**

145

146

### 147 **2.1 Sampling methods**

148

149 Water samples were collected at approximately two-degree intervals at 32  
150 stations from the *R/V Knorr* for trace metal determinations during GA03, the U.S.  
151 GEOTRACES expeditions, which took place between October 15 and November 4,  
152 2010 (USGT2010: KN199-04: 7°N to 17°N along 22°W) and between November 6  
153 and December 11, 2011 (USGT2011: KN204-01/02: 70°W to 25°W) in the North  
154 Atlantic Ocean. Sampling stations are shown in Figure 1. The first cruise (USGT10)  
155 started in Lisbon, Portugal and went south along 22°W, and then from the  
156 Mauritanian coast to the Cape Verde Islands (the Mauritanian transect, shown in  
157 Figure 1c). The second cruise (USGT11) started from Woods Hole, MA, USA and  
158 followed the repeat hydrographic section (Line W) southeast of Cape Cod, to  
159 Bermuda, and from there continued across the Atlantic ending at a repeat of Station  
160 USGT10-10 near the Cape Verde Islands.

161

162 Water samples were obtained using the custom-built U.S. GEOTRACES trace  
163 metal clean rosette which consists of an epoxy-painted aluminum rosette frame  
164 containing 24 x 12 L GO-FLO bottles (Cutter and Bruland, 2012). Before deployment  
165 and immediately upon recovery, the tops of the GO-FLO bottles were covered with

166 plastic shower-caps, and the bottles were removed from the frame and carried into  
167 the GEOTRACES clean van for sub-sampling. The GO-FLO bottles were pressurised  
168 to 10 psi using filtered compressed air, and samples were filtered through 0.2 µm  
169 Acropak filters that had been pre-cleaned by soaking overnight in filtered surface  
170 seawater that had been acidified to pH 2 using trace metal clean HCl, after which  
171 they were flushed with 5L of un-acidified, 0.2 µm-filtered surface seawater and  
172 stored empty in the refrigerator until use. All sub-sampling was undertaken in the  
173 clean van using rigorous trace metal protocols. Also, surface samples were collected  
174 using an underway towed-fish near-surface pumped seawater system (Johnson et  
175 al., 2007), and samples were sequentially filtered in-line at less than 8 psi through  
176 0.45 µm Osmonics and then a 0.2 µm polycarbonate track etched (PCTE) pleated  
177 filter cartridges.

178

## 179 **2.2 Analytical methods**

180

181 Seawater samples, collected at the full-depth stations and at demi stations  
182 (which only sampled the upper 1500 m for a more limited number of parameters),  
183 were drawn into pre-numbered 125 ml polymethylpentene (PMP) plastic bottles  
184 after three rinses and were stored in double plastic bags in the dark at room  
185 temperature before the Al determination, which was usually within 12 -36 hours of  
186 collection. Prior to analysis, samples for dissolved aluminium (dAl), were acidified  
187 by the addition of 125 µl sub-boiling distilled 6N HCl (hereinafter 6N HCl), and then  
188 they were microwaved in groups of 4 for 3 minutes in a 900 W microwave oven to  
189 achieve a temperature of  $60\pm 10^{\circ}\text{C}$  to release dissolved Fe, reported by Hatta et al.,  
190 (this volume). Subsamples were run on board ship within 24 hours of collection  
191 using the Flow Injection Analysis (FIA) method of Resing and Measures (1994). The  
192 detection limits and the precision of dAl for each cruise were as follows: 1.02 nM  
193 and 1.94% at 17.58 nM for the USGT10 cruise, and 0.24 nM and 4.8% at 1.67 nM for  
194 the USGT11 cruise.

195

196 In order to develop a coherent data set where values between different  
197 research groups can be compared, GEOTRACES has designated crossover stations  
198 where data can be obtained by different oceanographic groups. The Bermuda time  
199 series station S (BATS, Figure 1) is a crossover station for the North Atlantic, and  
200 data have been obtained at this station by both the NIOZ group (Royal Netherlands  
201 Institute for Sea Research, R. Middag., pers. comm.) in June, 2010 and the UH group  
202 in November, 2011.

203

204 Although both sets of data appear to be internally consistent and show  
205 smooth trends with depth, we note differences in the concentrations obtained by  
206 these two labs at this station (NIOZ data not shown as they are currently  
207 unpublished). The differences in the upper water column are likely a result of the  
208 seasonal difference (June vs November) and the ~1.5 year time difference in  
209 occupation of this station. Also, the different shape of the profiles at the very  
210 bottom of the two profiles appears to be the result of different conditions in the  
211 nepheloid layer at the time of sampling, but we do not have access to NIOZ  
212 transmissometer data. However, between 974 and 4002 m where we might expect  
213 to see consistency in Al concentrations over 1.5 years the two sets of data are offset  
214 and a cross plot of the data show that they fall on a well constrained line with little  
215 scatter ( $R=0.993$ ) suggesting a simple calibration offset between the methods. This  
216 offset varies from the UH data being ~2 nM higher at 1000 m (UH Al ~14 nM) to  
217 ~4.5 nM higher at 4,000 m (UH value ~30nM).

218

219 Both laboratories use the same chemistry for the analytical determination  
220 and are based on the Hydes and Liss (1976) lumogallion method. UH uses the  
221 method of Resing and Measures (1994) that was the original adaptation of the  
222 Hydes and Liss (1976) method to Flow Injection Analysis, and the NIOZ group uses a  
223 slightly modified version of this method that was published later by Brown and  
224 Bruland (2008). The main difference of that method from the Resing and Measures  
225 (1994) method is the use of a different resin for pre-concentration of the dissolved  
226 Al and the use of distilled water as the carrier instead of seawater.



227

228           The differences in concentration between the methods are not likely to be a  
229 result of random blanks as both methodologies produce smooth distributions that  
230 appear oceanographically consistent. Differences are also not likely to be the result  
231 of an un-recognised or overcorrected constant blank in either method as there is not  
232 a constant offset between the data sets, which would be expected in the case of a  
233 blank/blank correction problem.

234

235           We have also eliminated the possibility that this offset is a result of a problem  
236 with the UH standards by the following means. Shore-based re-analysis of the UH  
237 shipboard Al standards used during the USGT 2010 and USGT 2011 cruises, the  
238 original concentrated standards used to produce them and a newly purchased Al  
239 standard (SPEX, Assurance) show maximum differences of  $\sim 2.3\%$  from the  
240 expected values, which is close to the precision of the ICP MS measurements ( $\text{rsd}$   
241  $1\sigma=1.9\%$ ) used to inter-calibrate them. Thus, we believe that the UH data have been  
242 adequately verified by post-cruise ICP-MS calibration of our shipboard standards.  
243 Thus at this stage the cause of the offset is still unresolved.

244

245           However, regardless of the absolute differences between the reported values,  
246 the relative distributions are extremely similar. Thus, differences between the data  
247 sets affect absolute values, not the relative processes we describe and model here.  
248 They may however eventually provide insight into speciation and fractions of these  
249 metals in seawater and the importance of retaining shipboard standards and  
250 samples for future re-analysis.

251

252

## 253 **Results and discussion**

254

255

256           The cruise track and the general distribution of dissolved Al in the section  
257 are shown in Figs 1-4 produced using Ocean Data View (Schlitzer, 2013).

258

259           Our data show that there are three main sources of dissolved Al to the North  
260 Atlantic: atmospheric deposition of mineral dust and its partial dissolution in  
261 surface waters, inflow of dust-enriched Mediterranean outflow water (MOW) at  
262 approx 1200 m in the eastern basin, and input from the TAG hydrothermal vent site  
263 within the axial valley of the Mid Atlantic Ridge at ~3290 m. Additionally,  
264 resuspension of sediments in the energetic western boundary current leaves its  
265 mark on the northern source waters that flow around the periphery of the basin.  
266 We shall discuss the distribution of dissolved Al in terms of these sources and their  
267 interaction with advective processes in setting the large-scale distribution of  
268 dissolved Al in the North Atlantic. We will also examine the evidence for the  
269 hypothesis that vertical transport and remineralisation of dissolved Al associated  
270 with the biological Si cycle is responsible for these vertical distributions.

271

272           We will start with the surface waters since this tracks the input of dissolved  
273 Al from mineral dust deposition to the surface ocean and show that as a result of  
274 ventilation processes this signal can then penetrate into the oceanic interior. We will  
275 then examine the distribution in deeper layers.

276

### 277 **Surface waters**

278

279           As described in the introduction, the role that mineral dust deposition and its  
280 partial dissolution plays in adding dissolved Al to surface waters has been  
281 recognised by many investigators from some of the earliest studies. Building on  
282 these observations, Measures and Brown (1996) developed a simple one-box model  
283 that used the surface water dissolved Al signal to estimate dust deposition to the  
284 waters of the open ocean. This MADCOW model was subsequently validated with  
285 extensive data sets showing good agreement between the dissolved Al derived dust  
286 deposition estimates and those from independent sources such as land-based  
287 aerosol collections reported by Duce et al. (1991) and sediment trap records  
288 reported by a variety of workers and summarised by Measures and Vink (2000).

289 Since one of the world's major dust sources, the Sahara, is directly adjacent to the  
290 North Atlantic, surface dissolved Al values in this basin are amongst the highest seen  
291 in the open ocean.

292

293 The dissolved Al data in Figure 2, which are averages of all concentrations  
294 determined within the mixed layer (see below for mixed layer definition), shows  
295 values that range from ~9-45 nM Al. Overlain on the figure are the speed and  
296 direction of surface water flow at 30 m as recorded by the shipboard ADCP during  
297 the time of our station occupation.

298

299 Along the USGT11 cruise track, coastal values in the New England shelf are  
300 23-30 nM, with a large increase to ~45 nM coincident with the cruise track crossing  
301 into the Gulf Stream at USGT11-03 as shown in the overlain ADCP data (Figure 2).  
302 Higher values in the Gulf Stream are consistent with the Caribbean source of these  
303 waters, which is directly under the main plume of the Saharan dust (Husar et al.,  
304 1997). The values in the western edge of the Sargasso are somewhat lower than the  
305 Gulf Stream at 32-36 nM but build towards the centre of the gyre reaching a  
306 maximum of ~46 nM between 53 and 47°W. Values then drop rapidly towards the  
307 east, particularly around 36°W (USGT11-20) where the effect of the southward  
308 flowing Canary Current can be seen in the ADCP data. Values continue to drop  
309 reaching 19 nM at the Tenatso station USGT11-24. The equivalent occupation of  
310 this same station in 2010 (USGT10-12) showed somewhat lower surface water  
311 concentrations of ~15 nM Al. Continuation of the section towards the Mauritanian  
312 coast using the USGT10 data shows surface values increasing again as the ship's  
313 track encounters the coastal current and the upwelling regime directly under the  
314 Saharan plume. To the north along the USGT10 cruise track, Al concentrations  
315 decrease significantly as the track moves out of the Saharan plume with values  
316 dropping to ~9-11 nM at USGT10-1&2. A small region of higher values (20-23 nM)  
317 is seen at USGT10-5&6 which are situated to the west and downwind of the Canary  
318 Islands. The USGT10 cruise track overlaps part of the meridional CLIVAR A16N  
319 section (occupied in 2003) along ~25°W between ~31 to 17°N (Measures et al.,

320 2008). Despite the ~7-8 year gap in sampling times, very similar surface Al values  
321 (11-24 nM) are seen in this region, including an elevated region to the west of the  
322 Canary Islands, where values of 17-24 nM Al were also observed in 2003 (Measures  
323 et al., 2008).

324

325 The pattern of higher dissolved Al values seen in the central and western  
326 part of the sub-tropical gyre is similar to that seen in earlier surface water Al data  
327 sets reported by a variety of authors between 30 and 40°N and summarised by  
328 Measures et al. (2008). Thus, this pattern appears to be a relatively steady-state  
329 phenomenon for Al and is also similar to the geographical pattern of enrichment  
330 seen for several other dust-derived elements by GA03 cruise participants (Hatta et  
331 al., this volume).

332

### 333 **Dust deposition estimates**

334

335 The mixed layer dissolved Al values can be transformed into dust deposition  
336 estimates using the MADCOW model (Measures and Brown, 1996) which is a simple  
337 one box model that assumes that the existing dissolved concentration of Al in the  
338 mixed layer of the ocean is at a steady state between the competing process of  
339 partial dissolution of Al from mineral dust added to the surface ocean from the  
340 atmosphere, and scavenging removal onto particles exported from that surface  
341 layer. Implicit in this assumption is that the only source of Al to the surface ocean is  
342 from partial dissolution of mineral dust. In its simplest form the MADCOW model  
343 uses a fixed mixed layer depth of 30 m, a uniform surface water residence time of 5  
344 years, and assumes a solubility of 3.3%. In its application to this data set, we have  
345 adjusted these parameters to use the actual mixed layer depth we observed during  
346 our sections, which we define using a criterion of a 0.125 kg m<sup>-3</sup> difference in  
347 density between the surface samples and the bottom of the mixed layer (Hatta et al.,  
348 this issue). In addition to the density criterion, the temperature and salinity profiles  
349 were inspected at each station for uniformity within this layer, and if they were not  
350 uniform, the depth of any perturbation in the profile was chosen as the base of the

351 mixed layer. In addition we also calculate dust deposition along the 2003 CLIVAR  
352 A16N section to compare with the GA03 data.

353

354 The MADCOW calculated dust deposition along the USGT10 and USGT11  
355 cruise track ranges from 3.61 g m<sup>-2</sup> yr<sup>-1</sup> at USGT11-03 in the Gulf Stream to 0.91 g m<sup>-2</sup>  
356 yr<sup>-1</sup> at USGT10-02 off the coast of Portugal, with a broad area of deposition >3 g m<sup>-2</sup>  
357 yr<sup>-1</sup> in the centre of the subtropical gyre (Figure 3). While these values are within  
358 the ranges that have been reported for offshore waters in the tropical Atlantic (Duce  
359 et al., 1991), the spatial pattern they show is counter-intuitive, with higher values in  
360 the western and central basins despite the eastern Saharan source. Although  
361 deposition values increase along the track towards the African coast, reaching ~3 g  
362 m<sup>-2</sup> yr<sup>-1</sup> at USGT10-09, these values are lower than the geographical deposition  
363 estimates of Duce et al. (1991), the pattern from the shipboard dust collections  
364 (Shelley et al., this volume), and the relative abundance of particulate lithogenic  
365 material sampled from the water column with in situ pumps (Ohnemus et al., this  
366 volume). It is thus important to understand the underlying causes of these  
367 differences.

368

369 The first thing to note is that there are significant differences in the time  
370 scale that these signals represent. Shipboard aerosol sampling represents  
371 atmospheric loading during the cruise period, and the load of suspended particulate  
372 matter in the water column probably represents deposition to the ocean on a time  
373 scale of weeks to at most a few months. In contrast, dissolved Al, as a result of its  
374 residence time in surface waters (Jickells et al., 1994), is assumed to represent a  
375 moving average of dust input over an ~5 year period (Measures and Brown, 1996).  
376 It is this much longer time scale that is the root cause of the difference between the  
377 MADCOW and these other dust deposition estimates.

378

379 In the active upwelling region off Mauritania, the steady state assumption of  
380 the MADCOW model is not met because sub-surface water is providing 4-8 nM  
381 additional, non-aerosol Al to surface waters, thus leading to a 0.3-0.6 g m<sup>-2</sup> yr<sup>-1</sup>

382 overestimate of dust deposition in this area. However, competing with this  
383 overestimation is the likely underestimation of dissolved Al from dust input, since  
384 the upwelled water has not been at the surface for 5 years and therefore is not yet at  
385 steady state with the input. Since we do not know how long the water has been at  
386 the surface, we are not able to correct for this underestimate. Nevertheless,  
387 comparison with shipboard results and the Duce et al. (1991) estimates suggests  
388 that on balance the MADCOW approach is underestimating deposition in this area.

389

390 Similarly the assumed 5 year residence time of dissolved Al means that in  
391 advective regions the surface water will have moved considerable distances during  
392 this period (up to 3000 km at a velocity of  $10\text{cm s}^{-1}$ ). This is the underlying cause of  
393 the decreasing deposition estimates seen in the eastern part of the section between  
394 USGT11-16 & 24. This region corresponds to the ship's track crossing into the  
395 southward flowing Canary Current (Figure 2) that is bringing waters from the north,  
396 outside the main Saharan plume, and thus have been subject to less dust deposition.

397

398 Thus deposition values calculated from dissolved Al reflect an ~5-year  
399 running average of dust input into each square metre of surface water as it moves,  
400 not to a geographically static region in the manner of dust deposition maps derived  
401 from atmospheric data. Therefore, in regions affected by significant advection of  
402 surface water, this distribution will be different from that obtained from  
403 atmospheric sampling at fixed stations or from modelling efforts. While each  
404 estimate has its particular value in quantifying atmospheric processes, from an  
405 oceanographic perspective the imprint of dissolved Al in surface water is the most  
406 relevant parameter for understanding oceanic biogeochemical processes since it  
407 tracks the addition of dissolved materials to the surface water from dust deposition.

408

409

410 **Sub Tropical Mode Water**

411

412 In the subsurface waters of the western section between stations USGT11-08  
413 &15, (Figure 4, panel A), a region of enhanced Al, generally >30 nM, can be seen  
414 around 300 m corresponding to the 18° Sub-Tropical Mode Water (Worthington,  
415 1959). This high salinity, high dissolved O<sub>2</sub> water mass centred at  $\gamma^n = 26.5$ , which  
416 can also be identified by a local minima in the potential vorticity, forms in the late  
417 winter in the recirculation regime near the Gulf Stream (Talley et al., 2011), and  
418 through subduction carries the properties of the surface water into the interior of  
419 the Atlantic. Thus, the enhanced Al values seen in this water mass, which have been  
420 observed before in isolated stations (Measures et al., 1986) reflect the late winter  
421 surface water dissolved Al values, which are enhanced as a result of mineral dust  
422 deposition to this region. Diluted remnants of this subducted water mass can be  
423 seen stretching to the east of the MAR at the latitude of the USGT11 section to  
424 USGT10-5&6 (Figure 4, panel B) where a somewhat attenuated maximum in  
425 dissolved Al of ~27 nM can be seen associated with T, S and neutral density  
426 parameters that are very similar to those in the west. Although there is an eastern  
427 basin counterpart to the western basin 18° STMW, the Madeira Mode water (Siedler  
428 et al., 1987), which forms at the surface around 35°N south of the Azores Current  
429 front (Talley et al., 2011), we discount that this is the source of the eastern maxima  
430 for two reasons. The first is that the residence time of the Madeira mode water is  
431 ~9 months (Talley et al., 2011) and thus we would expect it to be almost completely  
432 dissipated given the ~8 month elapsed time between its late March formation time  
433 and our November sampling. Secondly, the surface water Al concentrations that we  
434 and others have observed in the area to the NW of Madeira where this water mass  
435 forms are much lower than the values we see in the STMW in this section (Siedler et  
436 al., 1987).

437

438

439 **The Mediterranean Outflow waters (MOW) and Antarctic Intermediate Water**  
440 **(AAIW)**

441

442 On the eastern boundary of the Atlantic in the N-S transect of the USGT10  
443 cruise (Figure 4, panel C), the dissolved Al data show a clear maximum at ~1200 m  
444 at stations USGT10-01 to 03 that is coincident with high salinity (contoured on top  
445 of the Al distribution) MOW entering the Atlantic. This water mass, which is a  
446 combination of Western Mediterranean Deep Water and Levantine Intermediate  
447 Water, exits through the shallowest, ~290 m deep Camarinal Sill at the Strait of  
448 Gibraltar and then sinks down the Atlantic slope, constantly entraining surrounding  
449 water to form a neutrally buoyant plume at  $\gamma^n = 27.5 - 27.9 \text{ kg m}^{-3}$ , centred at ~27.7  
450  $\text{kg m}^{-3}$ . This plume then spreads out along this isopycnal over large areas of the  
451 North Atlantic at a depth of approximately 1200 m. At our closest station to the  
452 outflow, USGT10-01, the maximum dissolved Al is 48 nM at a salinity of 36.503 and  
453 1186 m depth. A previous determination of the dissolved Al in the MOW outflow at  
454 the strait of Gibraltar (Measures and Edmond, 1988) reported values of ~71 nM Al  
455 at a salinity of ~38.1 at ~400 m. Since USGT10-01 is some ~400 km to the  
456 northwest of that 1986 station, we expect a more diluted signal of the outflow water  
457 as a result of the progressive entrainment of lower Al water into the MOW as it sinks  
458 to its neutral density surface at ~1200 m.

459

460 By station USGT10-05 at a latitude of 31°N, the salinity and Al maximum have  
461 been eroded from the vertical profiles at this depth as the MOW is now opposed by,  
462 and mixing with, the northward flowing low salinity, low Al AAIW on this neutral  
463 density layer. The AAIW, which forms in the South Atlantic between 45 and 50°S,  
464 has a salinity of ~ 33.8 and a potential temperature of 2.2°C at its point of origin. By  
465 the time it reaches the eastern side of the N Atlantic its core properties have been  
466 mixed with surrounding waters and the salinity minima values at USGT10-9&10 of  
467 34.91-34.94 and  $\theta = 6.0-6.5$  are seen at depths of 800-973 m. The influence of the  
468 AAIW diminishes rapidly to the north in the USGT10 section with the salinity  
469 minimum disappearing by USGT10-06 at 27°N. The salinity minimum of the AAIW  
470 can be traced along the  $\gamma^n = 27.7$  surface as it erodes westward across the basin in  
471 the USGT11 section, disappearing completely by USGT11-11 at ~60°W, where



472 southward flowing Irminger Sea Water (ISW) and upper Labrador Sea water take its  
473 place in this part of the water column. The AAIW is formed in the South Atlantic  
474 where dust deposition levels are low (Duce et al., 1991; Vink and Measures, 2001),  
475 and consequently the dissolved Al values of the AAIW in its formation region are  
476 also low. Dissolved Al data in the AAIW sampled in the Cape and Angola basins of  
477 the eastern S Atlantic (Measures, 1995) show Al values of ~2-3 nM at salinities of  
478 34.32 and 34.48.

479

480 A plot of all the Al data in the  $\gamma^n$  27.5 -27.9 density range from all the stations  
481 of USGT10 and all USGT11 station to the west of USGT11-11 (Figure 5), shows an  
482 extremely good correlation ( $R= 0.98$ ;  $n=83$ ) between the high salinity, high Al of the  
483 MOW and the low salinity, low Al water of the AAIW. If this correlation is  
484 extrapolated to a salinity value of 38.088, it predicts an Al value of 80.7 nM, slightly  
485 higher than the 72 nM value measured in the MOW in 1986 (Measures and Edmond,  
486 1988), which, as noted above, was not at the neutral density depth of the MOW  
487 plume, and thus might not be expected to fall on this mixing series. At the lower  
488 end, the predicted intercept of ~ 1 nM at a salinity of 34.4, is close to the 1995 Al  
489 value determined in the AAIW in the Cape Basin (Measures, 1995). The fact that  
490 these points fall so clearly on this mixing line with only minimal scatter we take as  
491 strong evidence that the distribution of dissolved Al in these waters is a result of a  
492 simple linear mixing between the MOW and AAIW end members. This result also  
493 reinforces the concept that at least along this density surface across the entire N  
494 Atlantic Basin there is no evidence for addition or removal of dissolved Al from the  
495 water column. In other words, the mixing process in this region of high atmospheric  
496 deposition to the surface waters and copious vertical transport by biological  
497 processes, is conservative, with no evidence of a remineralised Al signal. This  
498 conclusion is similar to that first reported by Measures and Edmond in 1990 based  
499 on the relationship between Al and salinity and Al and Si in the components of the  
500 lower NADW in the western basin of the North Atlantic when compared to values in  
501 the South Atlantic (Measures and Edmond, 1990)

502

503

504 **The waters of the New England shelf: USGT11-01-USGT11-11**

505

506 As described above, there is a distinct change in water masses at the  
507 boundary between USGT11-11 and USGT11-12 (Figure 4); however, the nature of  
508 the changes is more visible at the full depth station USGT11-10. At that station from  
509 ~950 m-1800 m,  $\gamma^n = 27.51-27.95$ , CFC levels are elevated, indicating the presence  
510 of recently ventilated waters (W. Smethie pers. comm.). Additionally, the  $\theta$ , salinity  
511 and silicate values indicate this water mass originated in the Labrador Sea. Dissolved Al  
512 values, in contrast, drop across this boundary, falling from 17-19 nM in the offshore  
513 gyre stations to 13-15 nM in the LSW and the shelf water stations. Although these  
514 values in the core of the Labrador Sea Water (LSW) USGT11-10 are relatively low  
515 compared to the gyre background, they are actually higher than the ~7 nM values  
516 reported in the filtered samples of LSW near its source at 55°N by Hall and Measures  
517 (1998). Here, we do see evidence of the addition of dissolved Al along the advective  
518 flow path of the LSW from its formation region in the Labrador Sea to the New  
519 England coast. This addition is consistent with the experimental and observational  
520 evidence presented by Moran and Moore (1991), who showed increased dissolved  
521 Al values in the near bottom waters off the Grand Banks of Nova Scotia, which they  
522 ascribed to inputs from resuspended sediments. It is also consistent with the  
523 concentration gradients seen in the various components of dissolved and colloidal  
524 Fe and dissolved Mn concentrations (Fitzsimmons et al., this issue; Hatta et. al., this  
525 issue). Thus, where we do see addition of dissolved Al to the water column, it is  
526 associated with sedimentary input along this advective flow path that follows the  
527 contours of the North American continental shelf in a region of extremely high  
528 resuspended material (Biscaye and Ettoreim, 1977).

529

530

531 **Hydrothermal inputs and their dispersal**

532

533 One of the most striking features of the data set is the clear source of  
534 dissolved Al at the MAR station USGT11-16 located close to the ~3620-3675 m deep  
535 TAG hydrothermal vent field (Figure 4C). At this station, high resolution sampling in  
536 the bottom 600 m was deliberately targeted to intersect the neutrally buoyant  
537 hydrothermal plume from this vent site. In addition to the normal sampling from  
538 the U.S. GEOTRACES trace metal clean rosette, we obtained additional samples from  
539 the regular hydrography rosette supplied by the Scripps Institution of  
540 Oceanography Ocean Data Facility (SIO ODF) that used standard 30 L Niskin bottles  
541 with internal springs to collect samples for non-contamination prone elements.  
542 Although there is clearly a danger of Al contamination of the samples from this  
543 system, our data (Figure 6) show that the elevated values seen by both sampling  
544 systems were very similar. Dissolved Al values in the plume reach 39-53 nM in the  
545 water column immediately above the hydrothermal vent site (depth range 3000-  
546 3595 m;  $\gamma^n$  range 28.06-28.08). These values are comparable to the 40-48 nM  
547 values reported for the TAG hydrothermal plume by Lunel et al. (1990) at an almost  
548 identical depth. Our deepest sample at 3587 m is some 87 m above the axial valley  
549 floor, which at this location is at 3674 m. While there are no reported  
550 measurements of dissolved Al in the hydrothermal end-member at the TAG vent  
551 site, there are other vents within the MAR that have been sampled and where both  
552 Al and Si were determined. Those values (Table 1) show end members (high  
553 temperature, undiluted vent fluid) that range from 1.8-5.3  $\mu\text{M}$  Al. Although this  
554 concentration range is large, the Si:Al ratio in these vents and also one from the  
555 21°N vent site are fairly constant at  $\sim 3,500 \pm 480:1$  (Si:Al mole:mole). Thus, using  
556 the determined Si end member value at TAG of 19-22 mM (Campbell et al., 1988;  
557 Rudnicki and Elderfield, 1992; Edmond et al., 1995), we can calculate a likely end  
558 member of  $\sim 5.4\text{-}6.3$   $\mu\text{M}$  Al.  $^3\text{He}$  concentrations determined in the neutrally  
559 buoyant plume at this station (W. Jenkins pers. com.), when compared to previously  
560 reported end member concentrations for TAG vent fluids (Rudnicki and Elderfield,  
561 1992), imply an  $\sim 50,000$ -fold dilution of the vent fluid by surrounding seawater  
562 leading to the formation of the neutrally buoyant plume. Thus, with a proposed vent

563 end member of  $\sim 6 \mu\text{M}$  Al we would expect an undetectable enrichment of  $\sim 0.1 \text{ nM}$   
564 Al in the plume over ambient values. Even if our end member estimate was low by a  
565 factor of 10, the neutrally buoyant plume enrichment would only be  $\sim 1 \text{ nM}$ , still  
566 barely detectable. In contrast, we see much higher enrichment values in the plume  
567 ( $\sim 11\text{-}19 \text{ nM}$  above background) when compared to stations on either side of the  
568 MAR.

569

570 Exactly why the TAG neutrally buoyant plume is so much more enriched in Al  
571 than would be predicted from its likely end member is beyond the scope of this  
572 manuscript. However, this phenomenon was previously observed by Lunel et al.  
573 (1990), who also observed very high concentrations of dissolved Al (up to  $62 \text{ nM}$ ) in  
574 the very bottom waters within  $140 \text{ m}$  of the TAG site. From their modelling of the  
575 entrainment process, they suggested that the entrainment of these Al-enriched near  
576 bottom waters could account for  $\sim 50\text{-}70\%$  of the Al anomaly observed in the plume.  
577 Our deepest samples show Al concentrations decreasing below the neutral density  
578 plume, but our sampling does not go deep enough to sample the very enriched  
579 bottom waters reported by Lunel et al., (1990).

580

581 The depth of the axial rift valley of the MAR is such that the neutrally buoyant  
582 plume at  $3,200 \text{ m}$  is constrained within the axial graben of the MAR, and thus the  
583 hydrothermal signals are to some degree trapped within this feature, perhaps  
584 allowing a much larger signal to develop than would otherwise be possible.  
585 Circulation and plume dispersal have been described in detail at the more northerly  
586 Rainbow Ridge (German et al., 1998), and the effects of tidal cycles on the plume at  
587 the TAG site have been described by Rudnicki et al. (1994). From these studies and  
588 others using naturally occurring radionuclides, German et al. (1991) have suggested  
589 that a large degree of mixing and re-entrainment of older plumes and re-  
590 replacement of particulate material that has precipitated from the neutrally  
591 buoyant plume can occur within these systems as the vertical density gradients  
592 within the graben are very weak. Thus, it might appear that the physical setting of

593 the vent sites within an enclosed axial valley on this slow spreading ridge is what  
594 leads to this Al enrichment.

595

596 Despite this plume trapping, the effects of the hydrothermal input are clearly  
597 visible in the water column to the west of the MAR in the nearest deep station  
598 (USGT11-14), where Al values of 31-33 nM can be seen from 3000 m to the bottom  
599 at 4230 m in the density range  $\gamma^n$  28.066 -28.125 (Figure 6, blue, and Figure 4). In  
600 addition to showing the known general westward flow at this depth (there is no  
601 equivalent enrichment at station USGT11-18 to the east of the MAR, Figure 6,  
602 purple), this also indicates that the enriched Al signal must be able to exit the axial  
603 valley of the MAR. However, it is important to note that the elevated values that we  
604 see to the west of the MAR are not necessarily from the TAG vent site. The  
605 frequency of venting along the MAR at this latitude (~1 vent every 130 km, German  
606 and Parson 1998), when coupled with the numerous transverse faults and the  
607 progressive deepening of the axial ridge to the south (Rona, 1977) provide ample  
608 opportunities for Al enriched seawater from a variety of such vents along the MAR  
609 to enter the deep waters at progressively deeper depths. This is particularly  
610 relevant when (below) we consider the potential for the Romanche and Vema  
611 Fracture Zones to be the likely source of enriched Al we see in the deeper waters of  
612 the eastern basin.

613

614 Thus, it is clear that hydrothermal processes in the Atlantic are significant  
615 contributors to dissolved Al in the deeper water column, in both the western basin  
616 and the eastern basin, as we elaborate below. It is noteworthy that this source was  
617 specifically excluded in the Atlantic Ocean Al model of van Hulst et al. (2013).

618

### 619 **The deep waters of the eastern basin**

620

621 The origin of the elevated dissolved Al in the eastern basin is of particular  
622 interest since the boundary currents in this basin are much weaker than those seen

623 in the western basin, and thus it is unlikely that resuspension of sediments can be  
624 the source. Instead we propose that the same Al plumes from hydrothermal venting  
625 that are elevating the Al in the deep waters of the western basin are also adding  
626 material to the eastern basin via mixing of these hydrothermally-influenced western  
627 basin water in the fracture zones.

628

629 The principal connections between the western and eastern basins of the  
630 tropical Atlantic occur through the 4,000 m deep Romanche and 4,700 m deep Vema  
631 Fracture Zones (FZ) that cut through the MAR ridge at 1° and 12°N, respectively  
632 (Heezen et al., 1964). These passageways provide a conduit for waters from the  
633 western basin (AABW and lower NADW) to ventilate this basin. A detailed set of  
634 transects in this region led McCartney et al. (1991) to suggest that it is the Vema FZ  
635 that is principally supplying the water that is ventilating the NE Atlantic Basin (~2  
636 Sv) and that the more southerly Romanche FZ situated at the Equator only supplies  
637 water to the basins south of the Sierra Leone Rise at ~ 8°N.

638

639 The deep passageways (~5,200 m) of the Vema FZ on the western side of the  
640 MAR allow the low temperature, high Si, northward flowing AABW to penetrate  
641 eastward across the MAR until they encounter the primary sill at ~41°W, 4,650 m  
642 where mixing with the overlying lower NADW occurs. This process then repeats at  
643 the secondary sill, 4,700 m (McCartney et al., 1991) further east at ~39° W, and both  
644 processes result in a jump in the bottom water temperatures and a reduction of Si in  
645 the bottom waters as the high Si, low T, AABW is mixed with the low Si, higher T,  
646 lower NADW. In a similar manner, we propose that low Al AABW from the western  
647 basin such as we see at the bottom of USGT11-12 (Figure 4), is mixed with Al  
648 enriched waters that have escaped the MAR axial valley as seen at the bottom of  
649 USGT11-14. These are mixed within the Vema FZ and delivered to the eastern  
650 basin, resulting in elevated Al values such as at USGT11-20.

651

652 While we do not have samples at the entrances and exits to Vema FZ, we can  
653 show the general feasibility of this process using the Si and Al data from our full

654 depth stations on either side of the MAR and using our deepest sampling in the  
655 AABW to provide the western basin end member at USGT11-12. The values used  
656 are shown in Table 2 and a simple cross plot (Figure 7) shows quite remarkably that  
657 such a mixture is a feasible solution to the source of the eastern basin Al. Although  
658 the deep water Al value at station 20 is clearly above this mixing line it is quite  
659 feasible that additional high Al water from the axial valley of the MAR could  
660 contribute dissolved Al to the mixture. Confirmation of this source would require a  
661 much higher resolution sampling in the region of this FZ than is possible in the  
662 GEOTRACES project.

663

664 We note that Klinkhammer et al. (1985) observed a plume of elevated Mn  
665 concentrations, indicating hydrothermal processes in the axial valley of the MAR at  
666 11°N very close to the Vema FZ, and that Fitzsimmons et al. (2013) also suggest a  
667 source of hydrothermal Fe to the eastern N Atlantic basin. Thus, it is very probable  
668 that there would be additional sources of dissolved Al in this region that could add  
669 to the waters flowing through the Vema FZ.

670

### 671 **The waters of the Mauritanian Shelf**

672

673 The intense oxygen minimum at USGT10-09 (Figure 8) where values as low  
674 as 45µM O<sub>2</sub> can be seen stretching to USGT10-12 in an attenuated form along  $\gamma^n =$   
675 27.1 is a result of the high productivity from upwelling along the NW African coast.  
676 The upper part of the dissolved Al minimum in this region (which is above the  $\gamma^n$   
677 layer of the AAIW mixing series) coincides very closely with this O<sub>2</sub> minimum. This  
678 indicates that in this intense depth range of biological remobilisation, under surface  
679 waters which receive large fluxes of Al from mineral dust deposition, there is no  
680 evidence of the release of dissolved Al to the water column through the  
681 remineralisation process. Furthermore in the deeper waters of these stations where  
682 high Si levels from benthic remobilisation are evident, the Si/Al ratio is completely  
683 different from that of the surface waters, in contrast to that which would be

684 expected from a biological remineralisation signal (Figure 8). Thus, this region  
685 which maintains one of the highest biological exports and also receives copious  
686 quantities of dissolved Al to the surface waters, shows quite distinctly that there is  
687 neither Al remineralisation associated with water column processes nor evidence  
688 for this process at the sediment water interface. These observations clearly call in  
689 to question the applicability of the van Hulst et al., 2013 model of these processes.

690

691

## 692 **Conclusions**

693

694

695 The dissolved Al distributions that we see in the zonal transect of the North  
696 Atlantic can be interpreted as resulting from a series of inputs and their  
697 redistribution by physical processes. At the surface of the ocean, partial dissolution  
698 of atmospherically-transported mineral dust labels all the surface waters of the  
699 North Atlantic to varying degrees, reflecting the amount of dust deposition they  
700 receive. This signal is carried into the sub-tropical mode water by the physical  
701 subduction of surface waters in late winter. A large input of Al enriched water from  
702 the Mediterranean outflow (that also originated from high dust deposition within  
703 that basin) can be seen mixing isopycnally with AAIW, with no evidence of dissolved  
704 Al addition or removal. Inputs of dissolved Al from resuspended sediments or their  
705 associated pore waters are evident along the advective flow path of the ULSW as it  
706 traverses the North American shelf. A significant dissolved Al input associated with  
707 the neutrally buoyant hydrothermal plume at the TAG MAR vent site can be seen  
708 escaping the MAR and labelling the deep waters of the western basin. The Al  
709 labelled western basin deep water when mixed with AABW is shown to be capable  
710 of producing the elevated values of dissolved Al seen in eastern basin waters. In the  
711 highly productive upwelling zone of the Mauritanian shelf, we see strong evidence  
712 of Al depletion by biological scavenging, but no evidence of its regeneration in either  
713 the oxygen minimum or at the bottom of the water column where Si is remobilised.

714



715

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717

718

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729

730

731

732 **References**

733

734

735 Bacon, M.P., and R.F. Anderson, 1982. Distribution of thorium isotopes between  
736 dissolved and particulate forms in the deep sea, *J. Geophys. Res.* 87, 2045-2056.

737

738 Biscaye, P.E., and S. L. Eittreim, 1977. Suspended particulate loads and transports in  
739 the nepheloid layer of the abyssal Atlantic Ocean, *Marine Geology*, 23,155-172.

740

741 Brown, M.T. and K. W. Bruland, 2008. An improved flow-injection analysis method  
742 for the determination of dissolved aluminum in seawater, *Limnol. Oceanogr.*  
743 *Methods*, 6, 87-95.

744

745 Campbell, A.C., M.R. Palmer, G.P. Klinkhammer, T.S. Bowers, J.M. Edmond, J.R.  
746 Lawrence, J.F. Casey, G. Thompson, S. Humphris, P. Rona, J.A. Karson, 1988.  
747 Chemistry of Hot Springs on the Mi-Atlantic Ridge, *Nature*, 335, 514-519.

748

749 Caschetto, S. and R. Wollast, 1979a. Vertical distribution of dissolved Aluminium in  
750 the Mediterranean Sea, *Marine Chemistry*, 7, 141-155.

751

752 Caschetto, S. and R. Wollast, 1979b. Dissolved aluminium in interstitial water of  
753 recent marine sediments, *Geochim. Cosmochim. Acta*, 43, 425-428.

754

755 Cutter, G.A., and K.W. Bruland, 2012. Rapid and noncontaminating sampling system  
756 for trace elements in global ocean surveys. *Limnol. Oceanogr. Methods* 10, 425-436.

757

758 Duce, R.A., and 21 others, 1991. The atmospheric input of trace species to the world  
759 ocean. *Global Biogeochemical Cycles*, 5, 193-259.

760

761 Edmond, J.M., A.C. Campbell, M.R. Palmer, G.P. Klinkhammer, C.R. German, H.N.  
762 Edmonds, H. Elderfield, G. Thompson, and P. Rona, 1995. Time series studies of vent  
763 fluids from the TAG and MARK sites (1986, 1990) Mid-Atlantic Ridge: a new  
764 solution chemistry model and a mechanism for Cu/Zn zonation in massive sulphide  
765 orebodies, *Hydrothermal Vents and Processes* (L.M. Parson, C.L. Walker, and D.R.  
766 Dixon, eds.), Geological Society Special Publication No. 87, 77-86.

767

768 Fitzsimmons, Jessica N., Ruifeng Zhang, Edward A. Boyle, 2013. Dissolved iron in the  
769 tropical North Atlantic Ocean, *Marine Chemistry* 15487-99.

770

771 German, C.R., A.P. Fleer, M.P. Bacon, and J.M. Edmond, 1991. Hydrothermal  
772 scavenging at the Mid-Atlantic Ridge: radionuclide distributions. *Earth and*  
773 *Planetary Science Letters*, 105, 170-181.

774

775 German, C.R., K.J. Richards, M.D. Rudnicki, M.M. Lam, J.L. Charlou, and the FLAME

776 Scientific Party, 1998. Topographic control of a dispersing hydrothermal plume,  
777 Earth and Planetary Science Letters, 156, 267-273.  
778

779 German C.R. and L.M. Parson, 1998. Distributions of hydrothermal activity along the  
780 Mid-Atlantic Ridge: interplay of magmatic and tectonic controls, Earth and Planetary  
781 Science Letters 160, 327-341.  
782

783 Hall, I., and C.I. Measures, 1998. The distribution of Al in the IOC stations of the  
784 North Atlantic and Norwegian Sea between 52° and 65° North, Marine Chemistry,  
785 61, 69-85.  
786

787 Heezen B. C., R. D. Gerard and M. Tharp, 1964. The Vema Fracture-Zone in the  
788 equatorial Atlantic, Journal of Geophysical Research, 69, 733-139.  
789

790 Hydes, D.J., and P.S. Liss, 1976. Fluorimetric method for determination of low  
791 concentrations of dissolved Aluminium in natural waters. Analyst 101, 922-931.  
792

793 Hydes, D.J., 1977. Dissolved aluminium concentration in sea water, Nature 268, 136  
794 - 137.  
795

796 Hydes, D.J., 1979. Aluminum in Seawater: Control by Inorganic Processes, Science,  
797 205, 1260-1262.  
798

799 Hydes, D. J., 1983. Distribution of aluminium in waters of the North East Atlantic  
800 25°N to 35°N, Geochim. Cosmochim. Acta, 47, 967-973.  
801

802 Hydes, D.J., P.J. Statham and J.D. Burton, 1986. A vertical profile of dissolved trace  
803 metals (Al, Cd, Cu, Mn, Ni) over the median valley of the Mid Atlantic Ridge, 43°N:  
804 implications for hydrothermal activity, Science of the Total Environment, 49,133-  
805 145.  
806

807 van Hulst, M.M.P., A. Sterl, A. Tagliabue, J.-C. Dutay, M. Gehlen, H.J.W. de Baar, and  
808 R. Middag, 2013. Aluminium in an ocean general circulation model compared with  
809 the West Atlantic Geotraces cruises, Journal of Marine Systems, 126, 3-23.  
810

811 Husar, R.B., J.M. Prospero, and L.L. Stowe, 1997. Characterization of tropospheric  
812 aerosols over the oceans with the NOAA advanced very high resolution radiometer  
813 optical thickness operational product, J. Geophys. Res., 102 16,889-16,909.  
814 (96JD04009).  
815

816 Jickells, T. D., T. Church, A. Veron, and R. Arimoto, 1994. Atmospheric inputs of  
817 manganese and aluminum to the Sargasso Sea and their relation to surface water  
818 concentrations, Marine Chemistry, 46, 283-292.  
819

820 Johnson, K.S., and 34 others, 2007. Developing Standards for Dissolved Iron in  
821 Seawater, EOS, trans American Geophysical Union, 88, 131.  
822

823 Klinkhammer G., P. Rona, M. Greaves, 1985. Hydrothermal manganese plumes in the  
824 Mid-Atlantic Ridge rift valley. *Nature* 314: 727-731.  
825

826 Lunel T., M. Rudnicki, H. Elderfield, D. Hydes, 1990. Aluminium as a depth-sensitive  
827 tracer of entrainment in submarine hydrothermal plumes, *Nature*, 344, 137-139.  
828

829 Mackenzie, F.T., M. Stoffyn, R. Wollast, 1978. Aluminum in Seawater: Control by  
830 biological activity, *Science*, 199, 680-682.  
831

832 McCartney, M.S., S.L. Bennett, M.E. Woodgate-Jones, 1991. Eastward flow through  
833 the Mid-Atlantic Ridge at 11°N and its influence on the abyss of the Eastern Basin. *J.*  
834 *Physical Oceanography*, 21: 1089-1121.  
835

836 Measures, C.I., 1995. The distribution of Al in the IOC stations of the South and  
837 Central Atlantic, *Marine Chemistry*, 49, 267-281.  
838

839 Measures, C. I., B. Grant, M. Khadem, D. S. Lee, J. M Edmond, 1984. Distribution of Be,  
840 Al, Se and Bi in the surface waters of the western North Atlantic and Caribbean,  
841 *Earth Planetary Science Letters*, 71, 1-12.  
842

843 Measures, C.I., J.M. Edmond, T.D. Jickells, 1986. Aluminium in the North West  
844 Atlantic, *Geochim. et Cosmochim. Acta*, 50, 1423-1429.  
845

846 Measures, C.I. and J.M. Edmond, 1988. Aluminium as a tracer of the deep outflow  
847 from the Mediterranean, *J. Geophys. Res.*, 93, 591-595.  
848

849 Measures, C.I. and J.M. Edmond, 1990. Aluminium in the South Atlantic: steady state  
850 distribution of a short residence time element, *J. Geophys. Res.*, 95, 5331-5340.  
851

852 Measures, C.I. and E.T. Brown, 1996. Estimating dust input to the Atlantic Ocean  
853 using surface water Al concentrations, in "The impact of African Dust across the  
854 Mediterranean" (Eds. Guerzoni and Chester) Kluwer, 389pp.  
855

856 Measures, C.I., and S. Vink, 2000. On the use of dissolved aluminium in surface  
857 waters to estimate dust deposition to the ocean, *Global Biogeochemical Cycles*, 14,  
858 317-327.  
859

860 Measures, C. I., W. M. Landing, M. T. Brown, and C. S. Buck, 2008. High-resolution Al  
861 and Fe data from the Atlantic Ocean CLIVAR-CO2 Repeat Hydrography A16N  
862 transect: Extensive linkages between atmospheric dust and upper ocean  
863 geochemistry, *Global Biogeochem. Cycles*, 22, GB1005, doi:10.1029/2007GB003042.  
864

865 Middag, R., H.J.W. de Baar, P. Laan, K. Bakker, 2009. Dissolved aluminium and the  
866 silicon cycle in the Arctic Ocean, *Marine Chemistry* 115, 176–195.  
867

868 Middag, R., H.J.W. de Baar, P. Laan, P.H. Cai, and J.C. van Ooijen, 2011. Dissolved  
869 manganese in the Atlantic sector of the Southern Ocean. *Deep Sea Research Part II*  
870 58:2,661–2,677, [http:// dx.doi.org/10.1016/j.dsr2.2010.10.043](http://dx.doi.org/10.1016/j.dsr2.2010.10.043).  
871

872 Moore, R.M., and G.E. Millward, 1984. Dissolved-particulate interactions of  
873 aluminium in ocean water. *Geochim. Cosmochim. Acta* 48, 235–241.  
874

875 Moran, S.B., and R.M. Moore, 1991. The potential source of dissolved aluminium  
876 from resuspended sediments to the North Atlantic Deep Water. *Geochim.*  
877 *Cosmochim. Acta* 55, 2475–2751.  
878

879 Moran, S.B., and R.M. Moore, 1992. Kinetics of the removal of dissolved aluminium  
880 by diatoms in seawater: A comparison with thorium. *Geochim. Cosmochim. Acta* 56,  
881 3365–3374.  
882

883 Oriens, K. J., and K. W. Bruland, 1985. Dissolved aluminum in the central North  
884 Pacific, *Nature*, 316, 427-429.  
885

886 Oriens, K. J., and K. W. Bruland, 1986. The biogeochemistry of aluminum in the  
887 Pacific Ocean, *Earth Planet. Sci Lett.*, 78, 397-410.  
888

889 Resing, J. and C.I. Measures, 1994. Fluorimetric determination of Al in seawater by  
890 FIA with in-line preconcentration, *Anal. Chem.*, 66,4105-4111.  
891

892 Rona, P. A., 1977. Paleobathymetry if the crest of spreading ridges related to the age  
893 of ocean basins-comment, *Earth Planet. Sci. Letts.*, 35, 454-456.  
894

895 Rudnicki, M.D, and H. Elderfield, 1992. Helium, radon and manganese at the TAG and  
896 Snake-pit hydrothermal vent fields, 26-degrees and 23-degrees-n, Mid-Atlantic  
897 Ridge, *Earth Planet. Sci Letts.* 113, 307-321, 1992. doi: 10.1016/0012-821.  
898

899 Rudnicki, M.D., R.H. James. H. Elderfield, 1994. Near-field variability of the TAG non-  
900 buoyant plume, 26N Mid-Atlantic Ridge, *Earth Planet. Sci. Lett.* 127.  
901

902 Schlitzer, R., *Ocean Data View*, <http://odv.awi-bremerhaven.de> , 2013.  
903

904 Siedler, G., Kuhl, A. and Zenk, W., 1987. The Madeira mode water, *J. Phys. Oceanogr.*,  
905 **17**, 1561-1570, 1987.  
906

907 Siedler, G., A. Kuhl, and W. Zenk, 1987. The Madeira mode water, *J. Phys. Oceanogr.*,  
908 17, 1561-1570.

909

910 Stoffyn, M. and F.T. Mackenzie, 1982. Fate of dissolved Aluminum in the oceans,  
911 Marine Chemistry, 11, 105-127.

912

913 Talley, L.D., G.L. Pickard, W.J. Emery, J.H. Swift, 2011. Descriptive Physical  
914 Oceanography: An Introduction. 6<sup>th</sup> Ed, Academic Press, 543pp.

915

916 Vink, S. and C.I. Measures, 2001. The role of dust deposition in determining surface  
917 water distributions of Al and Fe in the South West Atlantic, Deep-Sea Research, 48,  
918 2787-2809.

919

920 Worthington, L.V., 1959. The 18° water in the Sargasso Sea, Deep-Sea Res. 5, 297-  
921 305.

922

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925 **Tables**

926

927 Table 1 Hydrothermal vent end member concentrations in the MAR and elsewhere

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Vent site	Si mM	Al $\mu$ M	Fe $\mu$ M	Si: Al mM: $\mu$ M
Mark 1	18.2	5.3		3433
Mark 2	18.3	5.0		3660
TAG	22		1530	
21N	17.5	5.2	1640	3365
Rainbow	6.3-7.1	1.8-2.9	24000	2445-3500

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932 Table 2 Values used for constructing the mixing series across the MAR

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Parameter	GT11-12 (AABW)	GT11-14 Western flank of MAR	GT11-20 Eastern Basin
Si $\mu$ M	53.8	42.75	48.1
Al nM	19.90	32.175	28.15

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### Figure captions

Figure 1. A. Position of the sampling stations during the US GEOTRACES North Atlantic Cruises: Blue 2010, Red 2011 overlaid with the principal surface currents. Inverted diamonds are full depth stations, filled circles are demi stations where sampling was limited to 1500 m.

Figure 2. Distribution of dissolved Al in the surface mixed layer along the cruise track with the shipboard ADCP 35m vectors during station occupation overlaid. Note different Al concentration scale for the expanded section.

Figure 3. Estimations of dust input to the surface waters during the US 2010 and 2011 GEOTRACES cruises and comparison with those estimated for the 2003 A16N CLIVAR cruise.

Figure 4. Dissolved Al distribution (nM) along the USGT10 & USGT11 cruise tracks. Panels A&B: upper 1,000 m, overlaid with contours of potential vorticity ( $10^{-6} \text{m}^{-2} \text{s}^{-1} \text{K kg}^{-1}$ ). Panels C & D: full depth section overlaid with neutral density ( $\text{kg m}^{-3}$ , panel C) and salinity (panel D).

Figure 5. Correlation between dissolved Al and salt in the mixing series of Mediterranean Outflow Water and Antarctic Intermediate Water between  $\gamma^v = 27.5 - 27.9 \text{ kg m}^{-3}$ . The large cross at 72 nM Al is the concentration of dissolved Al in the MOW outflow reported by Measures and Edmond, 1998, the small box at 2.5 nM is the value reported by Measures, 1995 for AAIW.

Figure 6. Concentration of dissolved Al at USGT11-14, 16 & 18 (in colour) showing the hydrothermal plume. All samples were collected with the GT rosette system except for USGT11-16 SIO (red), which were collected with the normal hydrographic rosette. Black circles are all the dissolved Al concentrations in the USGT11 and USGT10 zonal sections.

Figure 7. Dissolved Al and Si correlation plot demonstrating the feasibility of producing eastern basin water with characteristic dissolved Al and Si, such as seen at USGT11-20 by mixing of Al enriched Lower North Atlantic Deep Water sampled at USGT11-14 with Si enriched Antarctic Bottom Water sampled at the USGT11-12 as they pass through the Vema Fracture Zone.

Figure 8. A. Dissolved Al in the Mauritanian section overlain with  $\text{O}_2$  concentrations.  
B. The ratio of dissolved Si to Al in the Mauritanian section, overlain with  $\text{O}_2$  concentrations.



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## **Figures**

982 See attached Powerpoint file for greyscale and colour versions of figures