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## Dissolved aluminium in the ocean conveyor of the West Atlantic Ocean: Effects of the biological cycle, scavenging, sediment resuspension and hydrography

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### ABSTRACT

The concentrations of dissolved aluminium (dissolved Al) were studied along the West Atlantic GEOTRACES GA02 transect from 64°N to 50°S. Concentrations ranged from ~0.5 nmol kg<sup>-1</sup> in the high latitude surface waters to ~48 nmol kg<sup>-1</sup> in surface waters around 25°N. Elevated surface water concentrations due to atmospheric dust loading have little influence on the deep water distribution. However, just below the thermocline, both Northern and Southern Hemisphere Subtropical Mode Waters are elevated in Al, most likely related to atmospheric dust deposition in the respective source regions.

In the deep ocean, high concentrations of up to 35 nmol kg<sup>-1</sup> were observed in North Atlantic Deep Water as a result of Al input via sediment resuspension. Comparatively low deep water concentrations were associated with water masses of Antarctic origin. During water mass advection, Al loss by scavenging overrules input via remineralisation and sediment resuspension at the basin wide scale. Nevertheless, sediment resuspension is more important than previously realised for the deep ocean Al distribution and even more intensive sampling is needed in bottom waters to constrain the spatial heterogeneity in the global deep ocean.

This thus far longest (17,500 km) full depth ocean section shows that the distribution of Al can be explained by its input sources and the combination of association with particles and release from those particles at depth, the latter most likely when the particles remineralise. The association of Al with particles can be due to incorporation of Al into biogenic silica or scavenging of Al onto biogenic particles. The interaction between Al and biogenic particles can lead to the coupled cycling of Al and silicate that is observed in some ocean regions. However, in other regions this coupling is not observed due to (i) advective processes bringing in older water masses that are depleted in Al, (ii) unfavourable scavenging conditions in the water column, (iii) low surface concentrations of Al or (iv) additional Al sources, notably sediment resuspension.

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### 1. Introduction

Aluminium (Al) is one of the most abundant chemical elements on the planet. The average crustal abundance of Al is ~8.23% by weight, three times less than the 28.15% silicon (Si) in the earth's crust. Both elements Al and Si are key constituents of clay minerals and clays are major sedimentary components on land and at the seafloor.

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In the oceans the concentration of dissolved Al in seawater ranges from extremely low 0.1–0.5 nM in remote Antarctic Ocean subsurface waters (Middag et al., 2011b, 2012), to 174 nM in the deep waters of the (East) Mediterranean Sea (Chou and Wollast, 1997; Hydes et al., 1988; Rolison et al., in this issue). In comparison, the concentration of dissolved silicate ranges from <0.1 μM in the surface waters of oligotrophic gyres in the central temperate oceans, to as high as ~30 μM in the deep North Atlantic Ocean and even ~180 μM in the oldest deep waters of the North Pacific Ocean (Sarmiento and Gruber, 2006). Silicon is a bio-essential nutrient for diatoms, which comprise ~40% of ocean phytoplankton productivity (Roberts et al., 2007). Diatoms utilize dissolved silicate, mostly H<sub>4</sub>SiO<sub>4</sub>, for the construction of their external opaline (SiO<sub>2</sub>) frustules. Contrarily, for Al there is no known biological function.

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The GEOSECS programme in the 1970s has been very successful in the worldwide mapping of the distributions of the major nutrients silicate, nitrate and phosphate in the oceans (Bainbridge et al., 1981). In the southward flowing North Atlantic Deep Water (NADW) the moderate nutrient concentrations are slowly yet steadily increasing with the southward transport. However, they remain in distinct contrast with the very high nutrients in the northwards flowing Antarctic Intermediate Water (AAIW) and Antarctic Bottom Water (AABW). These classical nutrient distributions of the West Atlantic Ocean are now in all textbooks and well understood due to the combination of the Meridional Overturning Circulation (Van Aken, 2007; Worthington, 1976, 1981) or 'Deep Ocean Conveyor Belt' (Broecker, 1991) with the biological cycle of uptake by plankton in surface waters and remineralisation in deep waters (Redfield et al., 1963).

In context of the International Polar Year (2007–2008) GEOTRACES campaign, strong correlations between dissolved Al and silicate were found in the 200–2000 m depth range in the Arctic Ocean (Middag et al., 2009). This ocean and the seas north of Iceland are the major source for the North Atlantic Deep Water (NADW) (Rudels et al., 2000). In contrast, no Al–Si relationship exists in the Southern Ocean where the Al concentrations are extremely low and the silicate concentrations very high (Middag et al., 2011b). We hypothesised that along the pathway of the southward flowing NADW somehow the Al–Si relationship becomes lost presumably due to steady net scavenging removal of Al from the NADW (Fig. 1).

The basin-scale (100–10,000 km) observation of a relationship between Al and Si in some, but by no means all, of the ocean basins, does not necessarily provide insight in the underlying microscopic plankton scale mechanisms. Latter mechanisms can be threefold, as

well as any combination thereof. Firstly, it has been shown a trace amount of Al can become incorporated 'intrinsically' in the siliceous (opal) frustules of living diatoms (Gehlen et al., 2002). Secondly, Al may become absorbed by diatoms, or adsorbed on the outside of such opaline frustules (Li et al., 2013; Moran and Moore, 1988, 1992). Upon settling of dead diatoms debris and dissolution of the frustules, the intrinsic and/or sorbed Al also becomes partly dissolved again. Thirdly, any of the relatively heavy diatom frustules that have become incorporated in aggregates of biogenic debris (marine snow) will by their "ballast effect" enhance the export of such marine snow to the deep ocean (Armstrong et al., 2001). Upon remineralisation this marine snow, any Al associated with it, will likely yield an overall Al–Si relationship in deep waters.

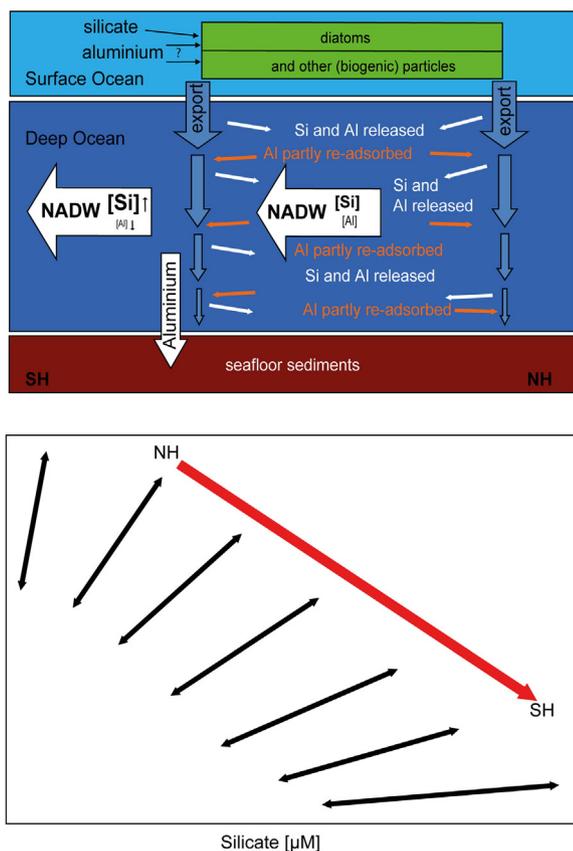
The campaign of four consecutive GEOTRACES cruises (2010–2012) in the West Atlantic Ocean offered the opportunity to unravel and elucidate the remarkable coupling and de-coupling of Al and Si in the Atlantic Ocean, and hence also assess the preceding hypothesis (Fig. 1). This paper presents the distribution, sources and sinks of subsurface Al along the West Atlantic section and details how the cycling of Al and Si can appear both coupled and uncoupled depending on the region. The surface distribution of Al and its use as a tracer of atmospheric dust input has been described separately to assist the interpretation of the distribution of iron (Rijkenberg et al., 2014) and cobalt (Dulaquais et al., 2014).

## 2. Methods

Samples were collected along the GEOTRACES GA02 Atlantic Meridional section of the Netherlands that consisted of 4 cruises (Fig. 2). Samples were collected using an all-titanium ultraclean CTD sampling system for trace metals (De Baar et al., 2008) with a new type of samplers constructed from PVDF (Rijkenberg et al., submitted for publication). A total of 60 depth profiles over the full water column were sampled, each comprising 24 sampling depths, resulting in 1439 samples for dissolved Al. Upon recovery, the complete CTD sampling system was immediately placed inside a clean room environment sampling container where the sub-samples for trace metal analysis were collected. The water was filtered from the PVDF samplers over a 0.2  $\mu\text{m}$  filter cartridge (Sartobran-300, Sartorius) under pressure (1.5 atm) of (inline pre-filtered) nitrogen gas. Henceforth, when referring to 'dissolved Al', this is operationally defined and includes colloidal Al smaller than 0.2  $\mu\text{m}$ . Sub-samples for dissolved Al were taken in cleaned (see (Middag et al., 2009) for cleaning procedure) LDPE sample bottles (125 mL) after five rinses with the sampled seawater. Samples for shipboard analysis were stored in a refrigerator (4 °C) and analysed usually within 24 h after sampling but always within 36 h.

Analyses of dissolved Al were performed on board with the improved lumogallion fluorescence flow injection method of Brown and Bruland (2008) with some minor modifications (Middag et al., 2011b). The samples of the 5 stations of cruise 64PE358 were measured in a shore based laboratory with the same method.

Samples were acidified to 0.024 M HCl (Baseline® Hydrochloric Acid, Seastar Chemicals Inc.) which results in a pH of  $\sim 1.8$ . The system was calibrated using standard additions from a 5000 nM Al stock solution to filtered acidified seawater of low Al concentration that was collected in the sampling area. A five-point calibration line and blank determination were made everyday. The resulting concentrations in nM were converted to  $\text{nmol kg}^{-1}$  based on the seawater density under lab circumstances. The blank was determined as the intercept of the signals of increasing pre-concentration times (30, 60, 120 and 240 s) of the calibration water and was 0.15 nM (SD = 0.035 nM;  $n = 57$ ). The value of 0.2 nM was the maximum allowed blank before starting a series of analyses. The limit of detection, defined as three times the standard deviation of the lowest concentration observed, was 0.05 nM. The flow injection system was cleaned every day by rinsing with a 0.5 M HCl solution. All samples were analysed in triplicate.



**Fig. 1.** Previously postulated hypothesis for changes in NADW while flowing southwards. Adsorptive scavenging causes continuous removal of Al from deep waters, while 'inert' dissolved Si only continues to increase due to dissolution of sinking diatom frustules. As a result the slope  $\Delta\text{Al}/\Delta\text{Si}$  decreases steadily while NADW travels from the Northern Hemisphere (NH) to the Southern Hemisphere (SH).

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