

Global Biogeochemical Cycles

Supporting Information

Trace element biogeochemistry in the high latitude North Atlantic Ocean; seasonal variations and volcanic inputs

Eric P. Achterberg^{1,2}, Sebastian Steigenberger^{1,3}, Jessica K. Klar⁴, Thomas J. Browning², Chris M. Marsay⁵, Stuart C. Painter³, Lucia Vieira², Alex R. Baker⁶, Douglas S. Hamilton⁷, Toste Tanhua², C. Mark Moore¹

¹Earth and Ocean Science, National Oceanography Centre Southampton, University of Southampton, Southampton SO14 3ZH, UK

²GEOMAR Helmholtz Centre for Ocean Research Kiel, 24148, Germany

³National Oceanography Centre, Southampton SO14 3ZH, UK

⁴Centre de Formation et de Recherche sur les Environnements Méditerranéens (CEFREM), UMR 5110, Université de Perpignan Via Domitia, CNRS, 66860 Perpignan Cedex, France

⁵Skidaway Institute of Oceanography, University of Georgia, Savannah, GA 31411, USA

⁶School of Environmental Sciences, University of East Anglia, Norwich, UK

⁷Department of Earth and Atmospheric Science, Cornell University, Ithaca, NY, USA

Corresponding author: Eric P. Achterberg (eachterberg@geomar.de)

Contents of this file

Text S1

Text S2

Figures S1 to S16

Tables S1 to S6

Introduction

This introduction provides further details of the analytical method used for trace element analysis in seawater, and water masses in the study region. In addition, a range of figures and tables are provided to support the narrative of the main manuscript.

S1 Analysis of trace elements in seawater

Concentrations of trace metals were determined by isotope dilution inductively coupled mass spectrometry (ID-ICP-MS), whilst the mono-isotopic elements Co and Mn were analysed using a standard addition approach followed by ICP-MS detection; all according to methods described in (Rapp et al., 2017). The ICP-MS analyses were conducted following an off-line preconcentration/matrix removal step (Rapp et al., 2017) on a WAKO chelate resin column (Kagaya et al., 2009). Briefly, in an acid cleaned 30 mL FEP bottle (Nalgene) 12 mL of the acidified sample was spiked with a standard solution containing the stable isotope ⁶²Ni, ⁶⁵Cu, ⁶⁸Zn, ¹¹¹Cd, ⁵⁷Fe and ²⁰⁷Pb (ISOFLEX, USA) which was enriched over its natural abundance. The exact concentration of the isotopically enriched trace elements in this standard solution was determined by ICP optical emission spectroscopy (OES). In addition, standard additions of Co and Mn were performed on subsets of seawater samples. After overnight equilibration the spiked samples were UV irradiated for at least 3 h and subsequently adjusted to pH 6.3 using ammonium acetate buffer, made from ultrapure acetic acid and ammonia (UpA, Romil, UK). The buffered sample was then pumped over the pre-concentration column, the column was rinsed with ultra high-purity water (UHP; MilliQ, Millipore, >18

MOhm cm) to remove salts, and subsequently the metals were eluted with 1 mL of 1 mol L⁻¹ HNO₃ (UPA; Romil, UK) and collected into acid cleaned polypropylene vials (4 mL; OmniVials) and capped. The pre-concentrated samples were analysed using an Element XR high resolution sector field inductively coupled plasma mass spectrometer (ThermoFisher) in low resolution (R=300) for ¹¹⁰Cd, ¹¹¹Cd, ²⁰⁷Pb, ²⁰⁸Pb, ⁹⁵Mo, ⁹⁶Mo and ¹¹⁵In and in medium resolution (R=4000) for ⁵⁶Fe, ⁵⁷Fe, ⁶⁰Ni, ⁶²Ni, ⁶³Cu, ⁶⁵Cu, ⁶⁶Zn, ⁶⁸Zn, ⁵⁹Co and ⁵⁵Mn allowing isobaric interferences (e.g. ⁴⁰Ar¹⁶O on ⁵⁶Fe) to be resolved. The samples were introduced via a 100 µL Teflon nebuliser connected to a quartz spray chamber. The trace element concentrations for Cd, Cu, Fe, Ni, Pb and Zn in the samples were calculated using a standard isotope dilution equation. The accuracy and precision of the method was assessed by analyses of SAFe (Sampling and Analysis of iron) reference samples (<http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials>). The values determined using the ID-ICP-MS method showed good consistency with the reported consensus values for the elements (Table S1). Dissolved Mn detected by ICP-MS yielded higher concentrations than the consensus values, in agreement with other observations that showed higher DMn concentrations obtained using ICP-MS analysis compared with catalytic-enhanced flow injection

(http://www.geotraces.org/images/stories/documents/intercalibration/Files/Reference_Samples_November11/SAFe_Ref_Mn.pdf).

All filtered water samples were analysed on board for dissolved Al between one day and one week after collection. Dissolved aluminium was determined by flow injection analysis with the lumogallion-Al fluorescence (FIA-FL) technique (Resing & Measures, 1994). Prior to analysis, acidified seawater samples were buffered to pH 5.2 ± 0.1 with ultraclean 2 M ammonium acetate buffer. This buffer was prepared using ammonium hydroxide (Romil, UpA) and acetic acid (Romil, UpA), diluted with milli-Q water and adjusted to pH 9.0 ± 0.1. The flow injection system automatically preconcentrated 7.5 ml of the buffered sample onto a column containing immobilized 8-hydroxyquinoline (8-HQ), which was subsequently rinsed with 3.75 ml of milli-Q water to remove interfering salts. In the following step, the Al was eluted from the 8-HQ column with 0.8 ml of 0.1 M HCl (Romil, UpA). The eluate of Al in HCl entered the reaction stream where it was mixed with a 58 µM lumogallion [3-(2,4-dihydroxyphenylazo)-2-hydroxy-5-chlorobenzenesulphonic acid] (MP Biomedicals) solution diluted in a 2 M ammonium acetate buffer solution (pH = 6.5 ± 0.1), which was prepared using the chemicals mentioned above. At a reaction pH of 5.9 ± 0.1, a fluorescing Al-lumogallion chelate is formed. The chelate was then mixed in a 15 m reaction coil placed in a water bath at 60 °C (Obata et al., 2000), followed by mixing with a 2.5 % Brij-35 (Sigma-Aldrich) solution (diluted in milli-Q water) in a 3 m long mixing coil to increase the sensitivity. Finally, the fluorescence of the chelate was measured on a RF-10A XL detector (Shimadzu), with a 484 nm excitation wavelength and a 552 nm emission wavelength. The resulting peak heights were recorded electronically for further processing. Each sample was measured in duplicate.

The analyses of aluminium in unfiltered samples (for TDAI) was carried out in the home laboratory one year after sampling, using a slightly modified FIA-FL protocol (Brown & Bruland, 2008)(Brown and Bruland, 2008). The acidified seawater samples were buffered to pH 5.2±0.1 in-line with a 2 M ammonium acetate buffer. The buffered sample was pre-concentrated onto a Toyopearl AF-Chelate-650M resin (contained in a Global FIA micro-column) and subsequently rinsed with 3.3 ml milli-Q water to remove interfering salts. Two pre-concentration volumes have been used for high concentration (3.3 ml) and low concentration (4.6 ml) samples of total dissolvable aluminium.

The dAl concentration measurements were calibrated with the use of standard additions from a 1000 ppm AAS standard solution (Sigma Aldrich) to filtered and acidified surface seawater of low Al concentration. A six-point calibration line in the range of sample concentrations was made for every analysis session or each time new reagents were prepared. Each standard addition was measured in duplicate. The buffer blank was corrected for by measuring a seawater sample containing double the amount of buffer (and brought back to the same sample pH by the addition of HCl) and subtracting from a normally buffered seawater sample. The buffer blank was typically relative to 0.2 to 0.5 nM Al and was subtracted from the peak height of every sample and standard measurements. The slope obtained from the standard additions after subtracting the double buffer difference was

then used to calculate Al concentrations of the measured samples. The limit of detection was 0.26 to 0.36 nM (defined as three times the standard deviation of the background variation) and the typical precision of analysed samples normally ranged from 1 to 8 %.

For quality control, sub-samples of a 25 L seawater sample were measured 16 times throughout the ship-board analysis sessions. The average concentration of this seawater was 4 nM with a standard deviation of 1 nM. Similarly, a seawater sample was measured 62 times during the TDAI analyses and was 12.9 nM with a standard deviation of 1.1 nM. Additionally, SAFe seawater samples (twelve times D2 and two times S) were also analysed several times, throughout the sample measurements. The average concentration for SAFe D2 (taken from bottles 379 and 421) was 1.0 ± 0.2 nM ($n = 4$), compared to the consensus value of 1.03 ± 0.09 nM (1 SD), and 1.88 ± 0.05 nM; $n = 3$ for SAFe S (taken from bottle number 599), compared to a reported consensus value of 1.67 ± 0.10 nM (1 D) (www.geotrac.es.org). The average concentration for the GEOTRACES intercalibration sample GD-132 was 18.5 nM with a standard deviation 0.9 nM ($n=5$), versus a consensus value of 17.7 ± 0.2 nmol/kg.

S2 Water mass distribution in study region

Features in the θ -S and OMP plots (Fig. S2 and S3) include Modified North Atlantic Water (MNAW) as part of the NAD, with enhanced salinities and temperatures, and contributing to >90% of waters shallower than ca. 800 m in the IB (Fig. S3). Subarctic Intermediate Water (SAIW), a mixture between MNAW and surface waters in the Labrador Current, typically constitutes the other water mass in this depth range of the water column (Fig. S3). Labrador Sea Water (LSW) is found below the MNAW and forms a dominant water mass which extends northward into the study area from the southern edge of the IB, at depths ranging from about subsurface to 2000 m in the IRB and 800 to 2000 m in the IB (Fig. S3), with θ of ca. 3-3.6°C and potential densities between 27.70 and 28.80 kg m⁻³. The Iceland-Scotland Overflow Water (ISOW) flows southwards at depth into the IB from the Arctic and is admixed with North Atlantic waters. The ISOW is present at depths below 1500 m (Fig. S3) and characterized by $\theta > 2$ °C ($S > 34.9$). The ISOW combines with the colder Denmark Strait Overflow Water (DSOW, S ca. 34.8, θ 0-1.4°C), both forming part of the North Atlantic Deep water (NADW). The DSOW is prominent in the IRB as a deep water mass below 2000 m (Fig. S3). The NADW is characterized by S 34.9-35.0 and θ 2.1-3.5°C (Fig. S2) and found in the IB and IRB at depths below 1000 m (Fogelqvist et al., 2003). Mediterranean Overflow Water (MOW), which features enhanced θ (ca. 13.5°C) and S (ca. 38.1), could only be detected at a number of southern stations in our study region, with a maximum contribution of 3-7%.

References

- Brown, M. T., & Bruland, K. W. (2008). An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. *Limnology and Oceanography-Methods*, 6, 87–95.
- Fogelqvist, E., Blindheim, J., Tanhua, T., Osterhus, S., Buch, E., & Rey, F. (2003). Greenland-Scotland overflow studied by hydro-chemical multivariate analysis. *Deep-Sea Research I*, 50(1), 73–102.
- Kagaya, S., Maeba, E., Inoue, Y., Kamichatani, W., Kajiwar, T., Yanai, H., et al. (2009). A solid phase extraction using a chelate resin immobilizing carboxymethylated pentaethylenhexamine for separation and preconcentration of trace elements in water samples. *Talanta*, 79(2), 146–152. <https://doi.org/10.1016/J.TALANTA.2009.03.016>
- Obata, H., Nozaki, Y., Okamura, K., Maruo, M., & Nakayama, E. (2000). Flow-through analysis of Al in seawater by fluorometric detection with the use of Lumogallion. *Field Analytical Chemistry and Technology*, 4(6), 274–282.

Rapp, I., Schlosser, C., Rusiecka, D., Gledhill, M., & Achterberg, E. P. (2017). Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry. *Analytica Chimica Acta*, 976. <https://doi.org/10.1016/j.aca.2017.05.008>

Resing, J. A., & Measures, C. I. (1994). Fluorometric Determination of Al in Seawater by Flow Injection Analysis with In-Line Preconcentration. *Geochim. Cosmochim. Acta* (Vol. 66). Retrieved from <https://pubs.acs.org/sharingguidelines>

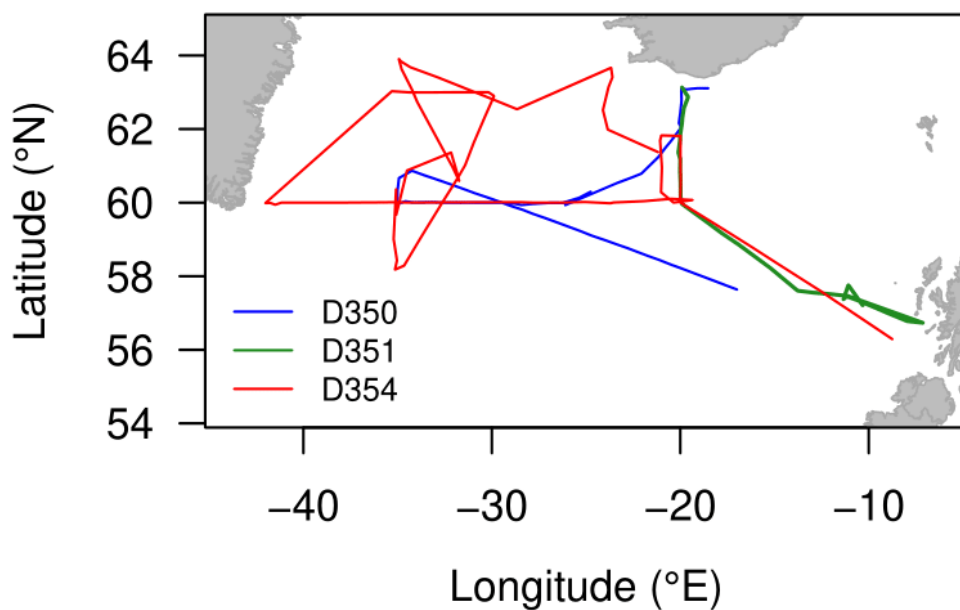


Figure S1: Cruise tracks of cruise D350 (in blue), D351 (in green) and D354 (in red). The cruises took place in spring and summer 2010 (Spring: April 26-May 9 (D350) and May 10-28 (D351); Summer: July 4-August 11 (D354)). Figure produced using R.

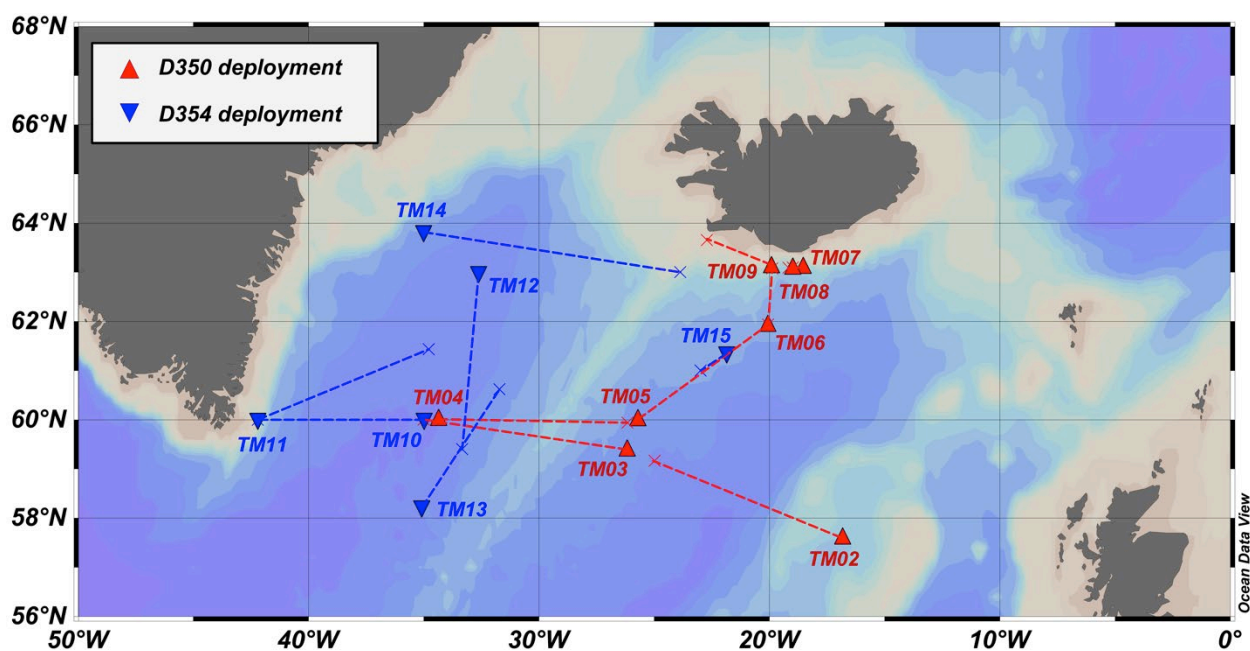


Figure S2: Aerosol sampling for D350 (red dotted line; spring cruise) and D354 (blue dotted line; summer cruise). Triangles indicate position where aerosol sampling commenced, and crosses where sampling finished. Figure produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

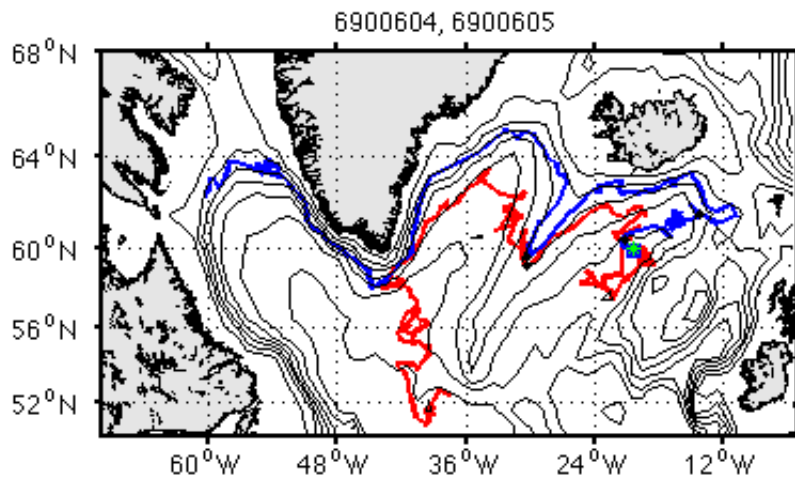


Figure S3: Argo float tracks following deployments in Iceland Basin in July 2007 (Cruise RRS Discovery D321). Release site indicated in green. Blue track for Provor track, and red track for Apex track. Figure was produced in Matlab (Version 2009a; <https://www.mathworks.com>) using the freely available mapping toolbox `m_map` (available at <https://www.eoas.ubc.ca/~rich/map.html>). The coastline database is the Global Self-Consistent, Hierarchical, High-resolution Geography Database (GSHHG; available at <https://www.ngdc.noaa.gov/mgg/shorelines/gshhs.html>) and based on Wessel, P., and W. Smith (A Global Self-consistent, Hierarchical, High-resolution Shoreline Database, *J. Geophys. Res.*, 101, 8741-8743, 1996). The bathymetry is from a 1 degree global bathymetric database included within the Matlab software (The disclaimer in the software notes the following "The topography data used in this demo is available from the National Geophysical Data Center, NOAA US Department of Commerce under data announcement 88-MGG-02"). Argo data was downloaded from <http://www.usgoda.gov/argo/argo.html>.

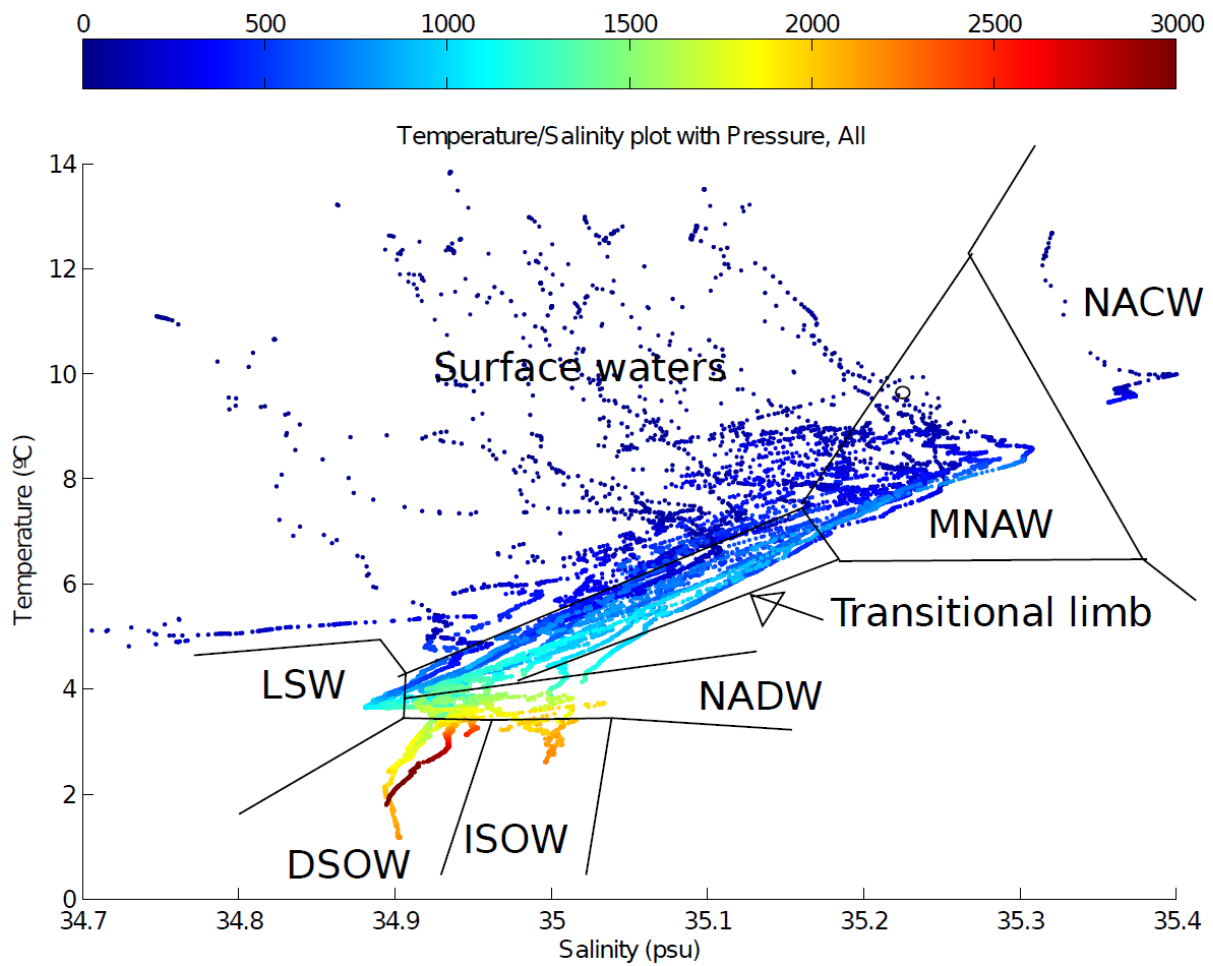


Figure S4. Potential temperature versus salinity plot for all D354 data. Colour on graph is depth (as pressure in dBar). Abbreviations: Denmark Strait Overflow Water (DSOW), Iceland-Scotland Overflow Water (ISOW), North Atlantic Deep Water (NADW), Labrador Sea Water (LSW), North Atlantic Central Water (NACW), Modified North Atlantic Water (MNAW).

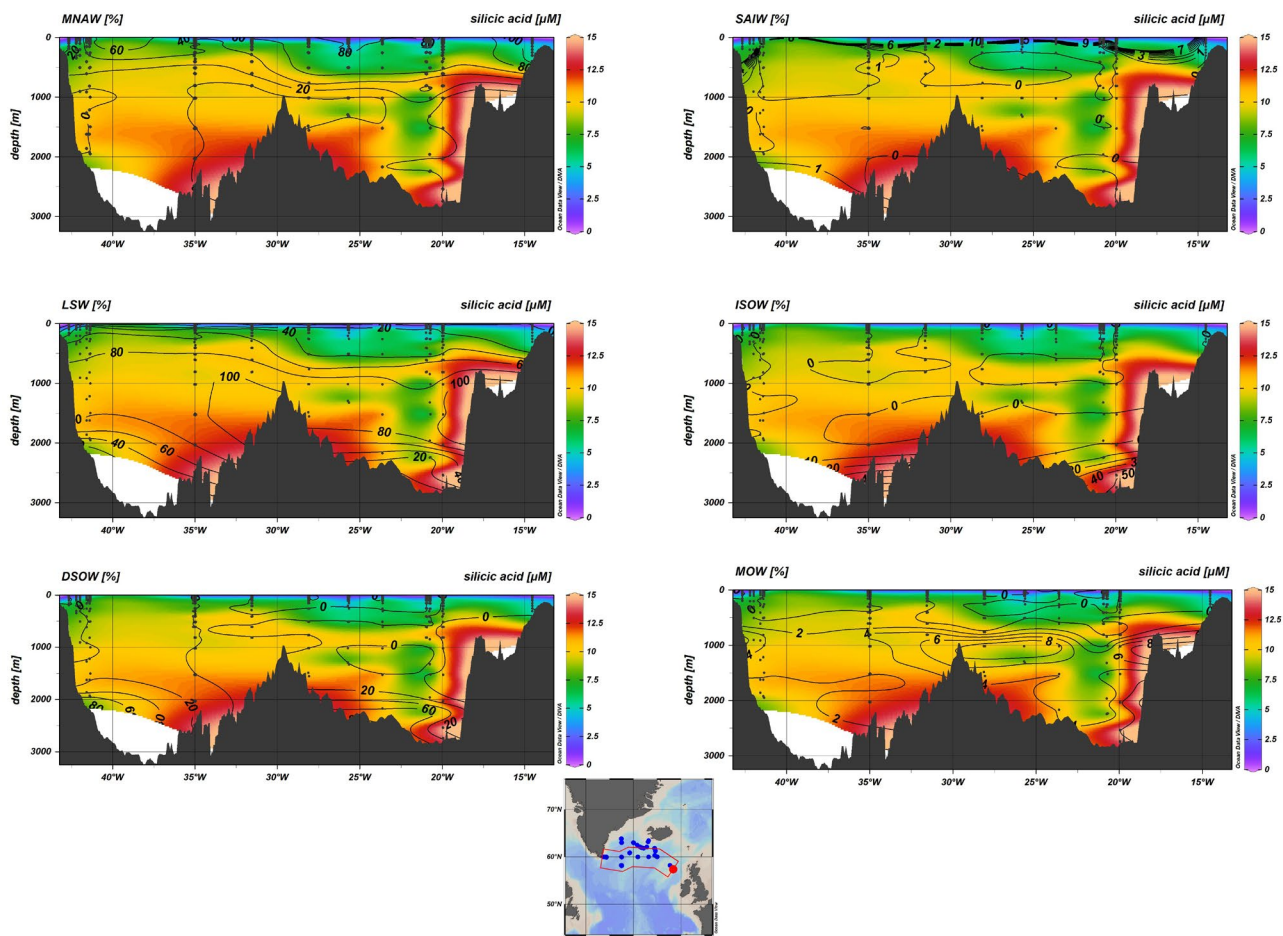


Figure S5: Silicic acid section along east-west section at 60°N with water masses indicated as percentage contributions. Water masses were obtained following OMP method by Tomczak (1999) using nutrient, salinity, oxygen and potential temperature data from this study to define water mass properties. MNAW: Modified North Atlantic Water; MOW: Mediterranean Overflow Waters; LSW: Labrador Seawater; ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water; SAIW: Subarctic Intermediate Water. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

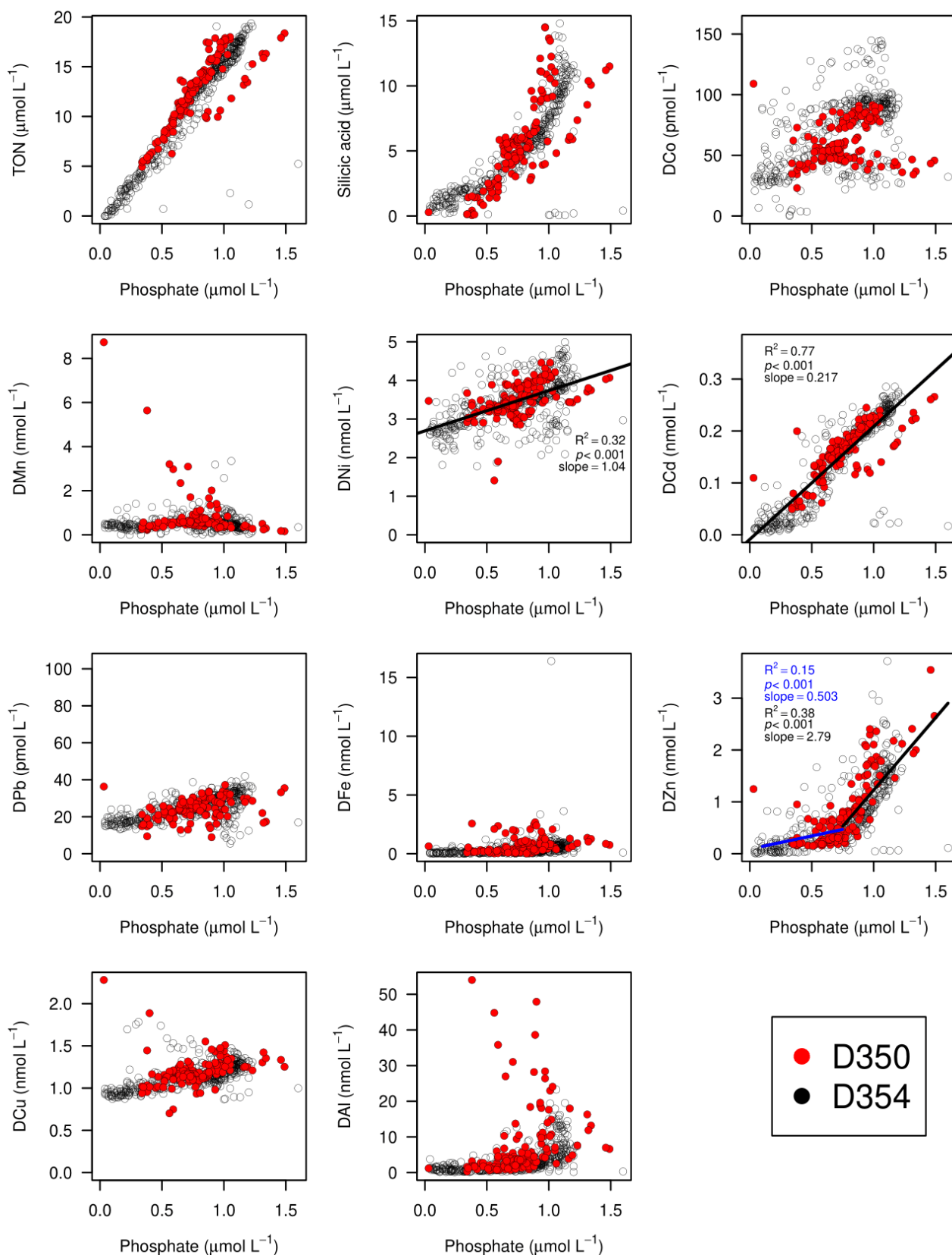


Figure S6: Plots of trace elements against phosphate for all data for cruise D350 and D354. Figures were produced using R. Regressions for DZn are divided at $0.75 \mu\text{M}$ phosphate.

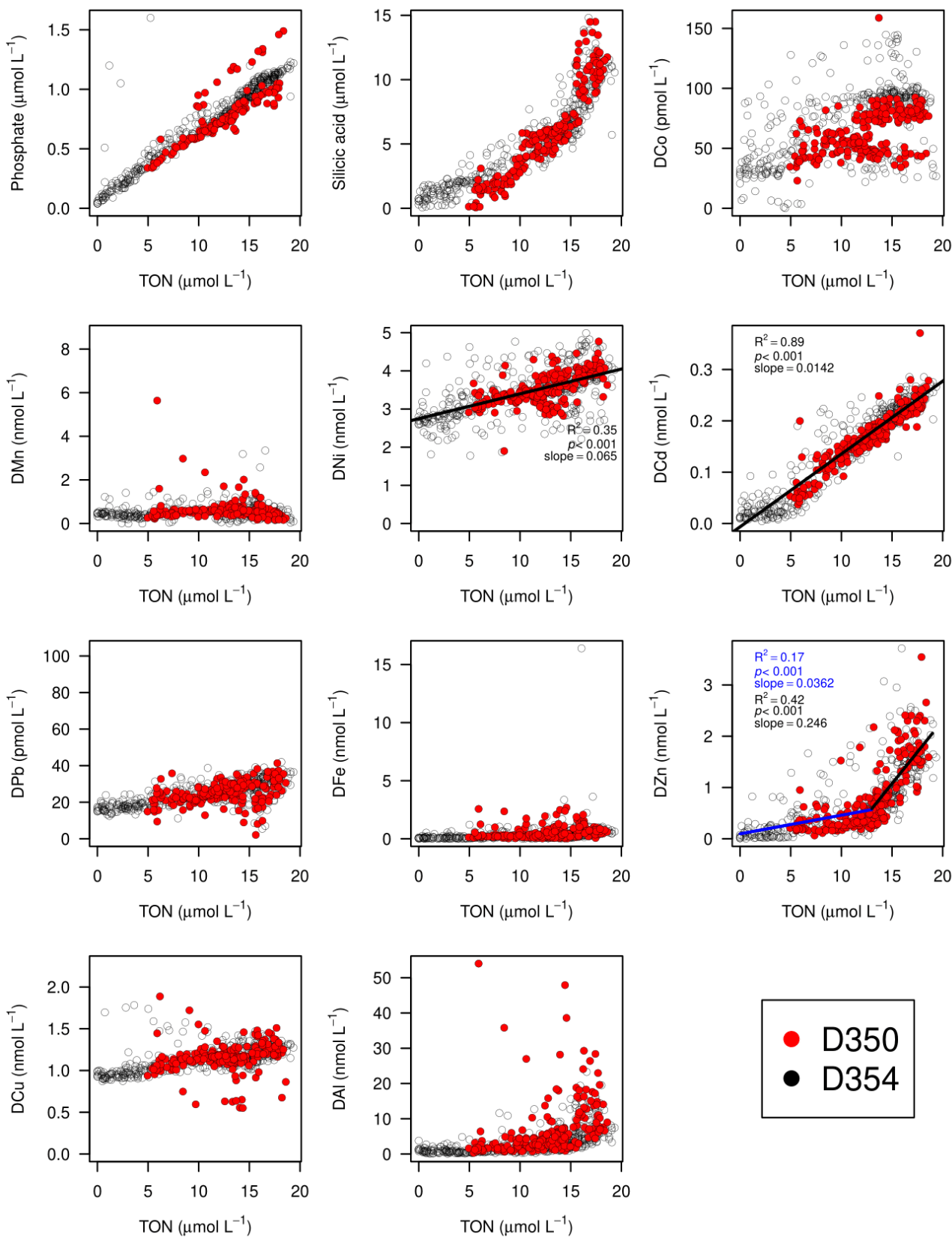


Figure S7: Plots of trace elements against nitrate+nitrite (TON) for all data for cruise D350 and D354. Figures were produced using R. Regressions for DZn are divided at $13 \mu\text{M}$ TON.

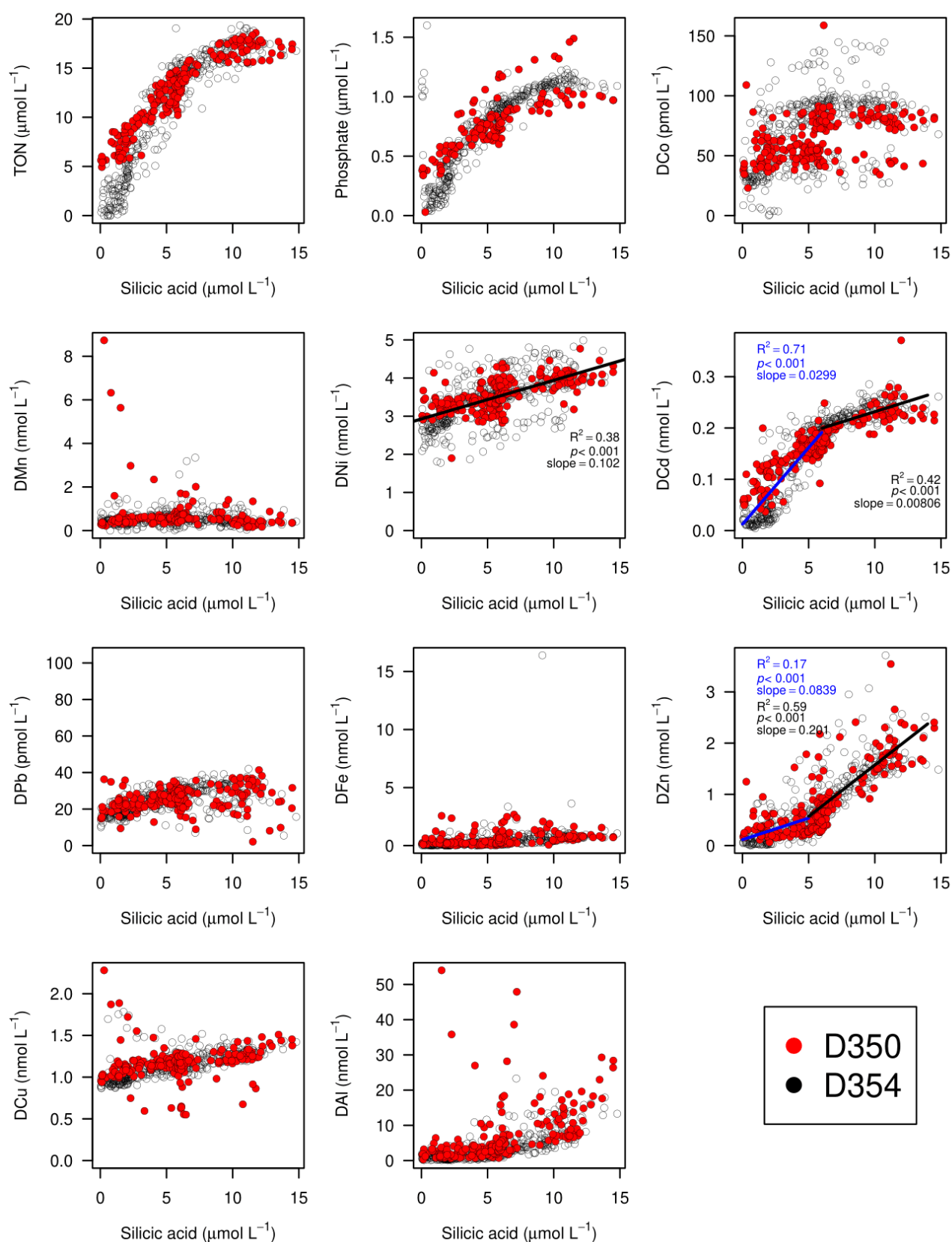


Figure S8: Plots of trace elements against silic acid for all data for cruise D350 and D354. Figures were produced using R. Regressions for DCd are divided at 6 μM silicic acid, regressions for DZn are divided at 5 μM silicic acid.

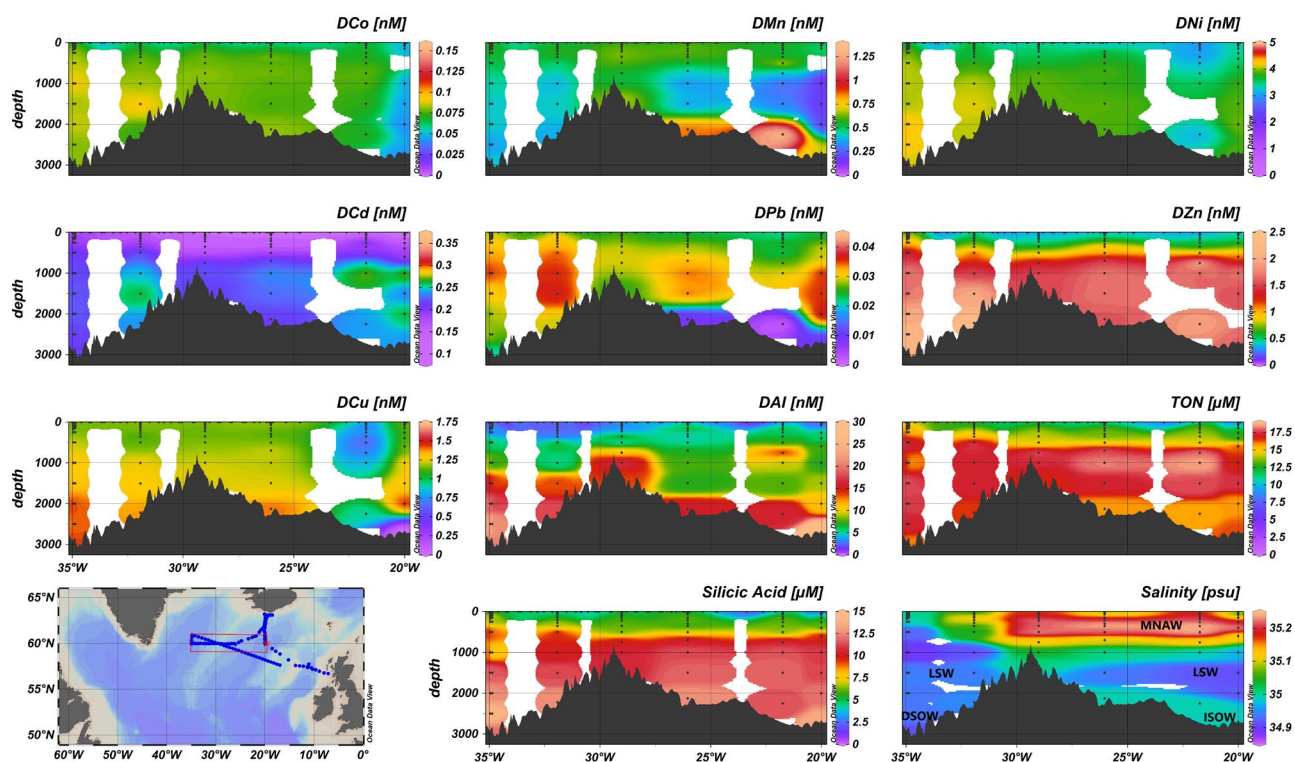


Figure S9: Section plots of dissolved trace elements, nitrate+nitrite (TON), silicic acid and salinity on a transect along 60°N with data from spring 2010. Main water masses indicated in salinity panel and explained in SI Text S2. MNAW: Modified North Atlantic Water; LSW: Labrador Seawater; ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

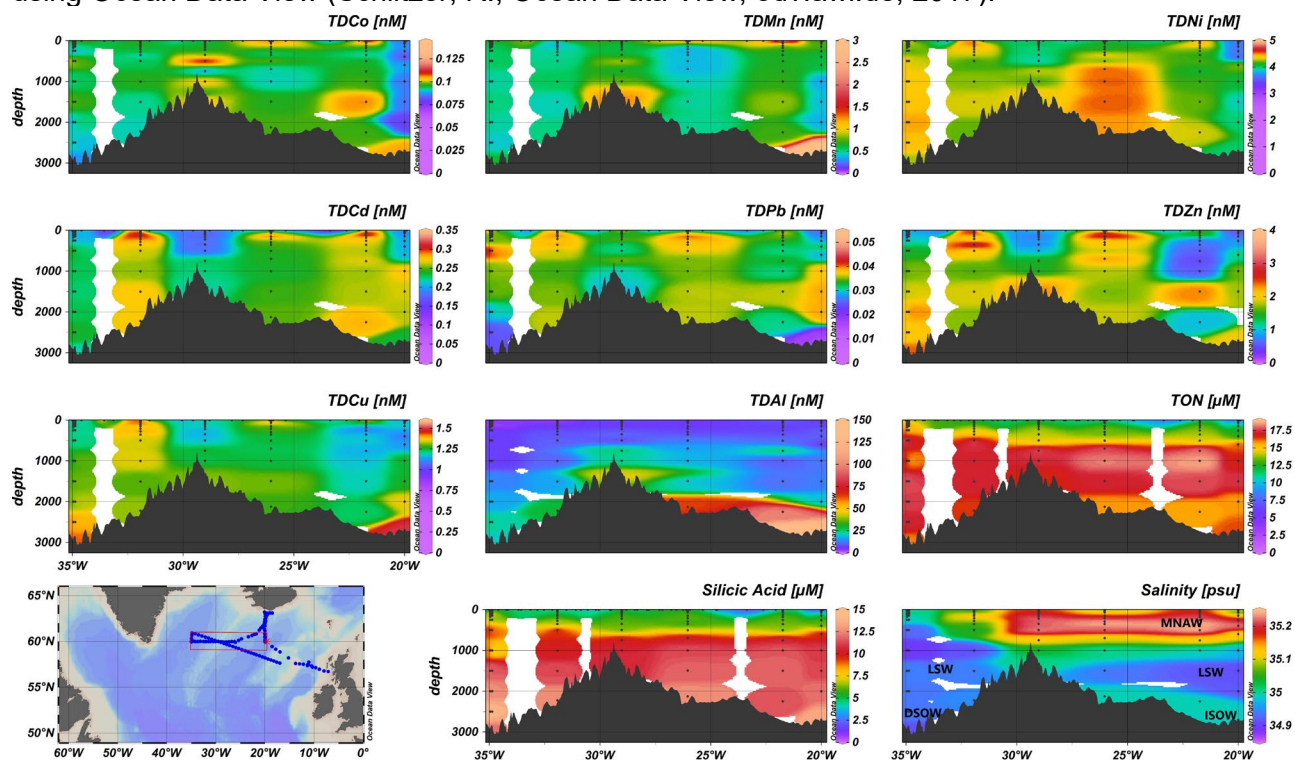


Figure S10: Section plots of total dissolvable trace elements, nitrate+nitrite (TON), silicic acid and salinity on a transect along 60°N with data from spring 2010. Main water masses indicated in salinity panel and explained in SI Text S2. MNAW: Modified North Atlantic Water; LSW: Labrador Seawater;

ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

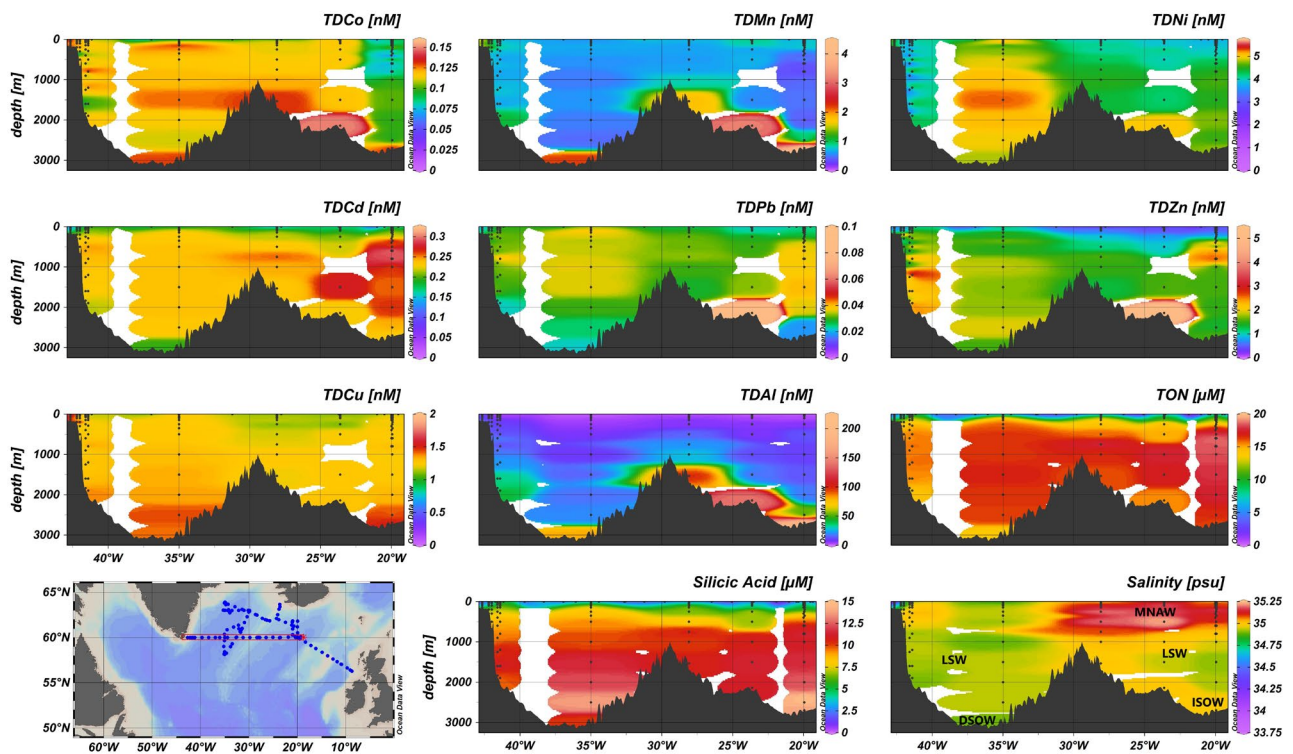


Figure S11: Section plots of total dissolvable trace elements, nitrate+nitrite (TON), silicic acid and salinity on a transect along 60°N with data from summer 2010. Main water masses indicated in salinity panel and explained in SI Text S2. MNAW: Modified North Atlantic Water; LSW: Labrador Seawater; ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

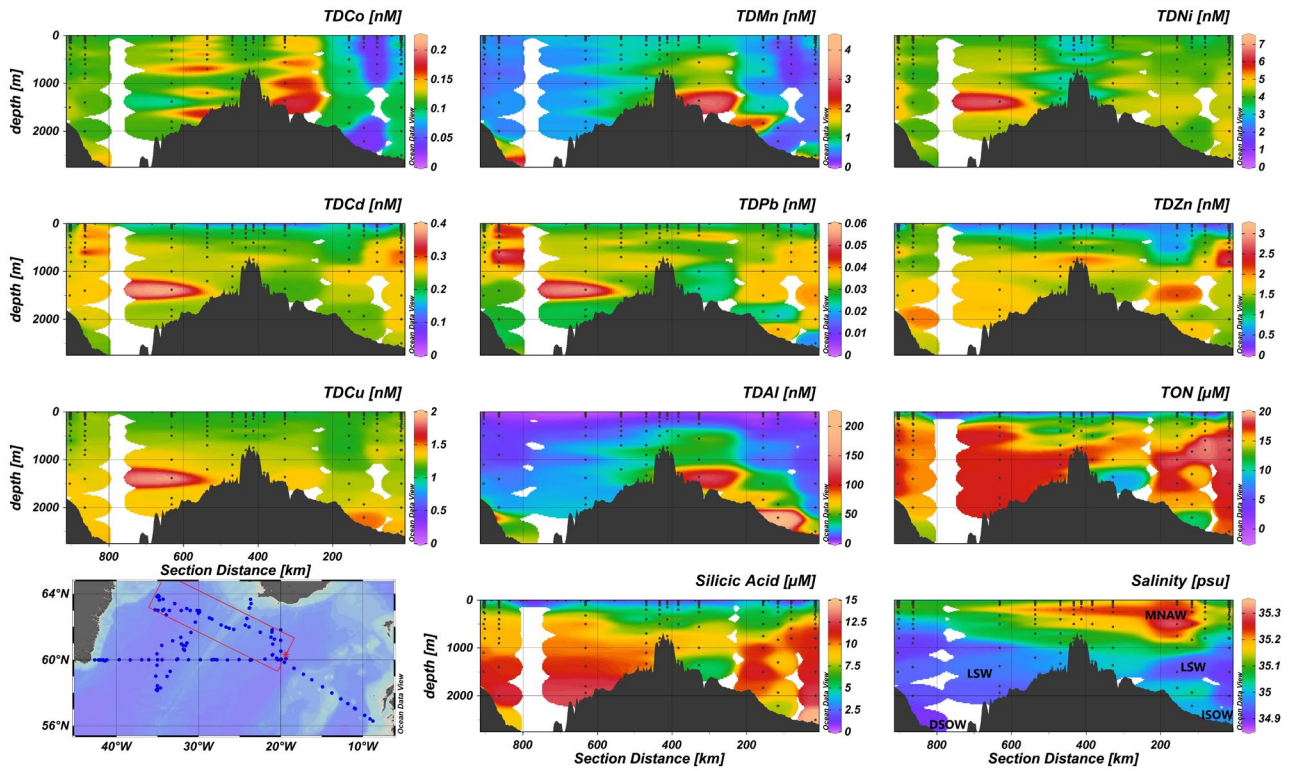


Figure S12: Section plots of total dissolvable trace elements, nitrate+nitrite (TON), silicic acid and salinity on a transect across the Reykjanes Ridge at 62°N with data from summer 2010. Main water masses indicated in salinity panel and explained in SI Text S2. MNAW: Modified North Atlantic Water; LSW: Labrador Seawater; ISOW: Iceland-Scotland Overflow Water; DSOW: Denmark Strait Overflow Water. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

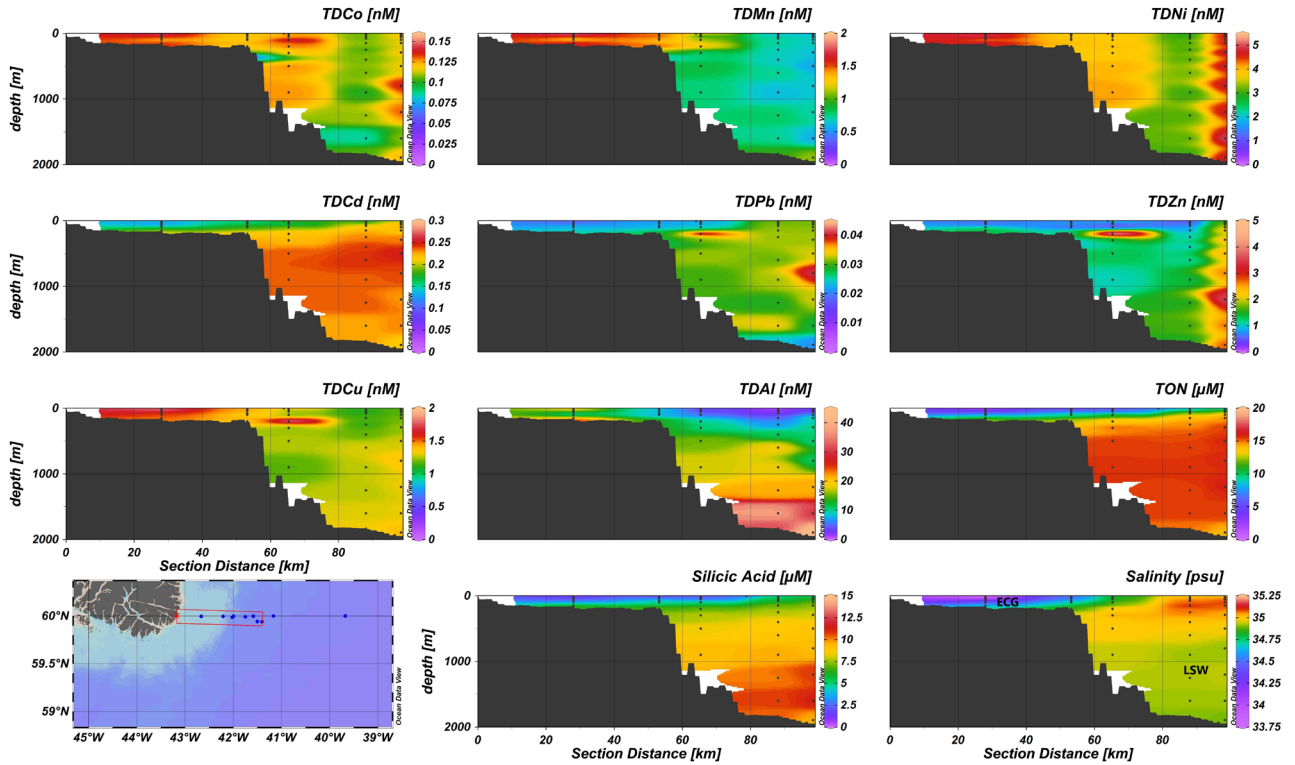


Figure S13: Section plots of total dissolvable trace elements, nitrate+nitrite (TON), silicic acid and salinity on a transect along 60°N onto the Greenland shelf with data from summer 2010. Main water masses indicated in salinity panel and explained in SI Text S2. ECG: East Greenland Current; LSW: Labrador Seawater. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

NOAA HYSPLIT MODEL
Backward trajectories ending at 1800 UTC 03 May 10
GDAS Meteorological Data

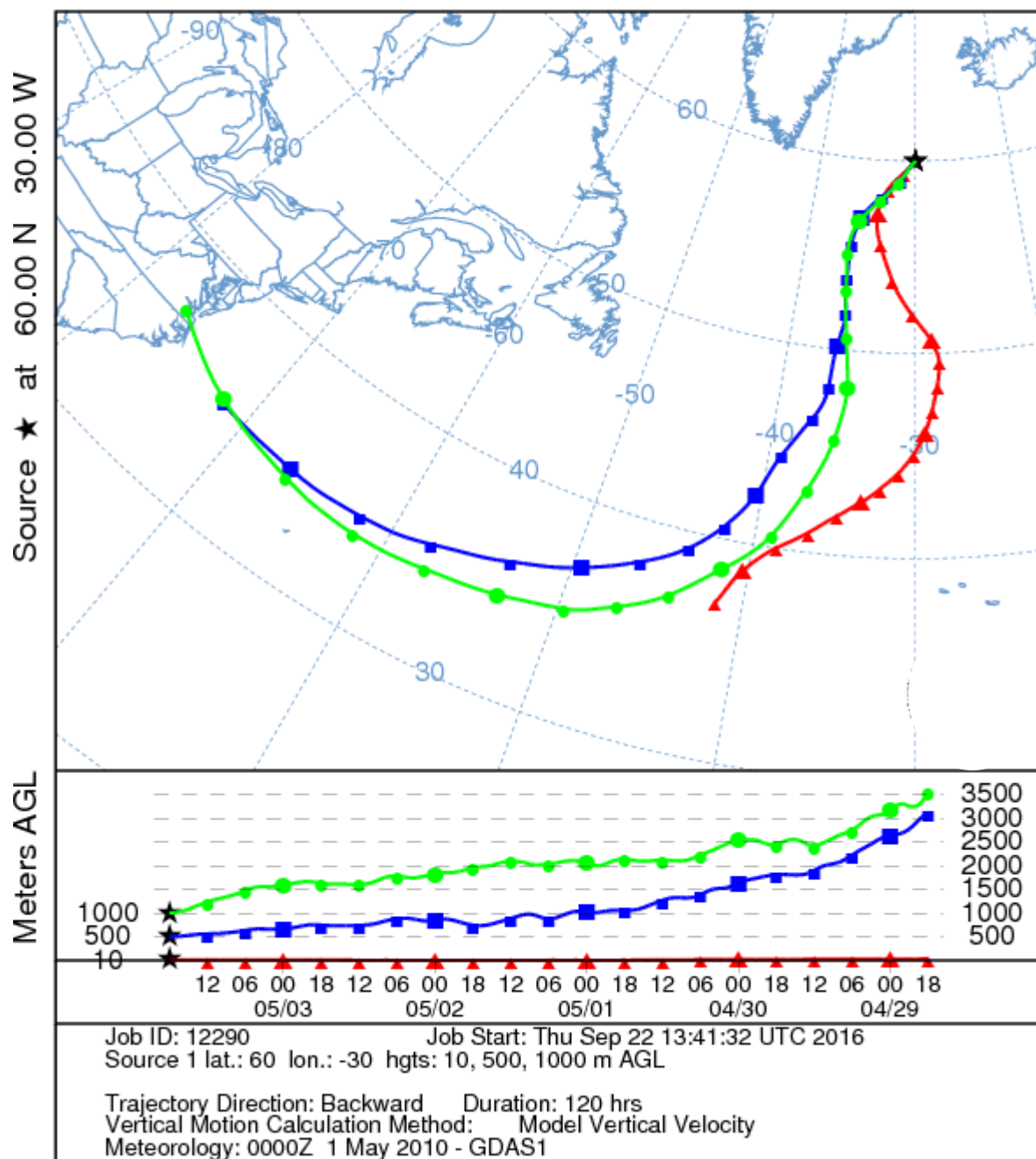


Figure S14: Airmass backtrajectories for 10, 500 and 1000 m height for a 5 day period ending May 3, 2010 (1800 h), related to the position of RRS *Discovery*. We acknowledge the US National Oceanic and Atmospheric Administration/Department of Commerce for the use of the Hysplit model and image.

NOAA HYSPLIT MODEL
Backward trajectories ending at 1500 UTC 05 May 10
GDAS Meteorological Data

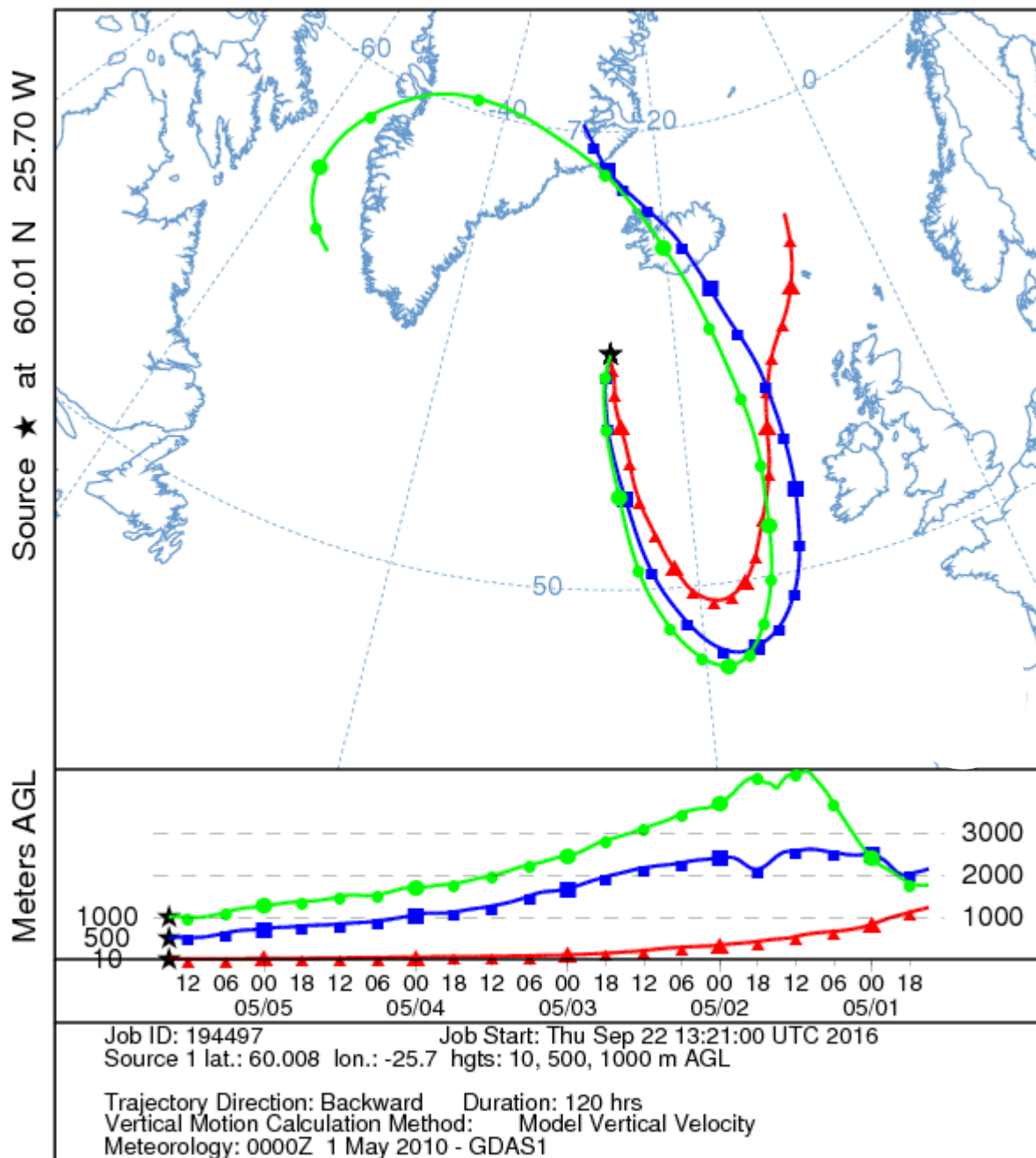


Figure S15: Airmass backtrajectories for 10, 500 and 1000 m height for a 5 day period ending May 5, 2010 (1500 h), related to the position of RRS *Discovery*. We acknowledge the US National Oceanic and Atmospheric Administration/Department of Commerce for the use of the Hysplit model and image.

NOAA HYSPLIT MODEL
Backward trajectories ending at 1600 UTC 08 May 10
GDAS Meteorological Data

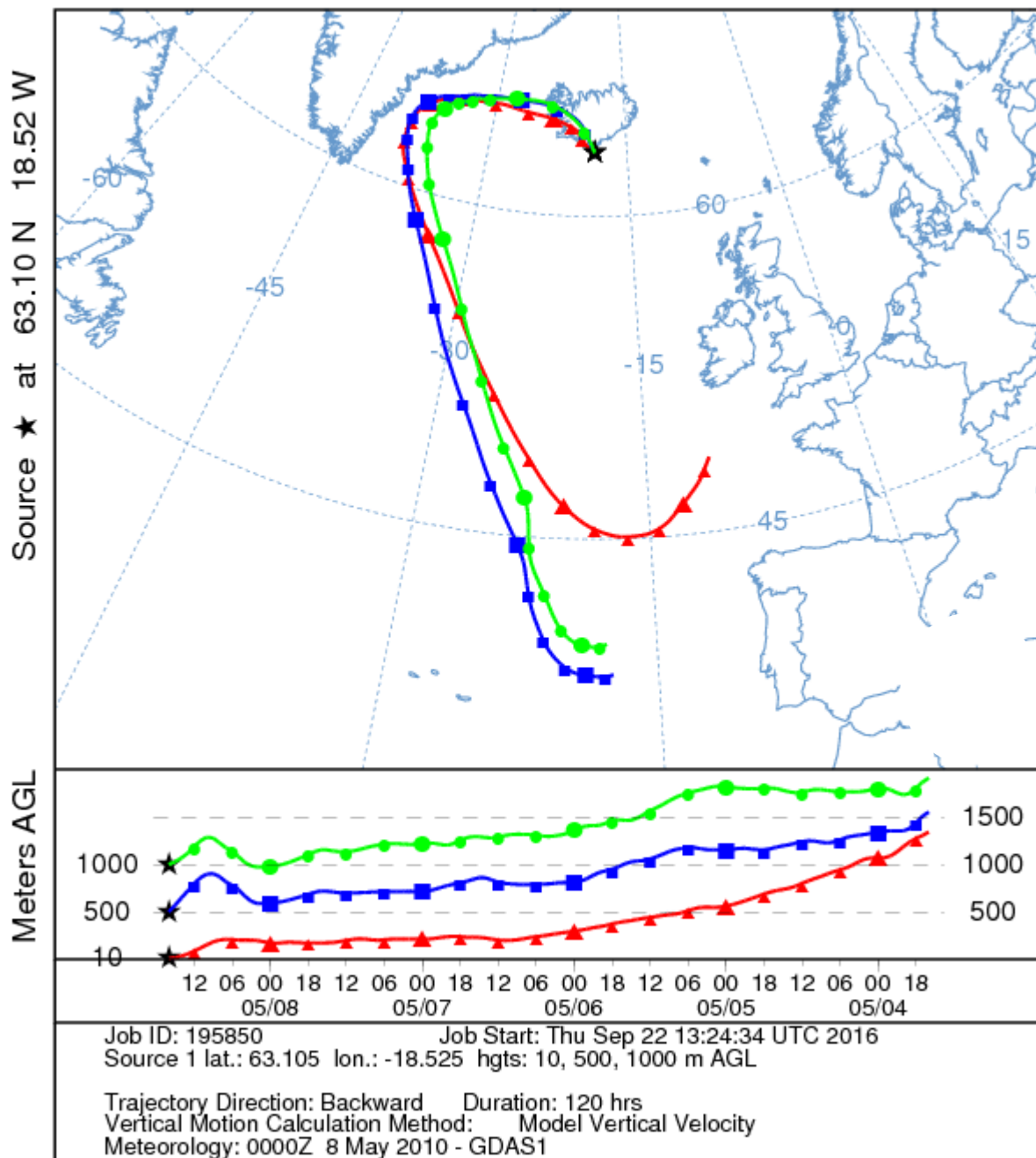


Figure S16: Airmass backtrajectories for 10, 500 and 1000 m height for a 5 day period ending May 8, 2010 (1600 h), related to the position of RRS *Discovery*. We acknowledge the US National Oceanic and Atmospheric Administration/Department of Commerce for the use of the Hysplit model and image.

Table S1 Results of analysis of consensus seawaters. SD is standard deviation.

[illegible]

Table S2. Characteristics used for Optimum Multiparameter water mass analysis method (Tomczak, 1999).

| Potential temp | salinity | oxygen | PO ₄ | NO ₃ | Si | Water Mass |
|----------------|----------|--------|-----------------|-----------------|------|--|
| 11.07 | 35.24 | 271 | 0.44 | 5.93 | 1.58 | Atlantic Water (AW) |
| 13.47 | 38.07 | 189 | 0.35 | 8.2 | 6.10 | Mediterranean Overflow Water (MOW) |
| 3.22 | 34.86 | 291 | 1.07 | 16.1 | 9.4 | Labrador Sea Water (LSW) |
| 2.69 | 34.96 | 272 | 1.11 | 16.6 | 15.9 | Iceland-Scotland Overflow Water (ISOW) |
| 1.37 | 34.88 | 299 | 1.10 | 14.1 | 8.9 | Denmark Strait Overflow Water (DSOW) |
| 5.14 | 34.78 | 270 | 1.05 | 16.0 | 8.9 | Subarctic Intermediate Water (SAIW) |

Table S3. Pearson correlations of data from cruises D350, D351 and D354.

| | <i>depth</i> | <i>TD</i> <i>Co</i> | <i>TD</i> <i>Mn</i> | <i>TD</i> <i>Ni</i> | <i>TD</i> <i>Cd</i> | <i>TD</i> <i>Pb</i> | <i>TD</i> <i>Fe</i> | <i>TD</i> <i>Zn</i> | <i>TD</i> <i>Cu</i> | <i>TD</i> <i>Al</i> | <i>DCo</i> | <i>DMn</i> | <i>DNi</i> | <i>DCd</i> | <i>DPb</i> | <i>DFe</i> | <i>DZn</i> | <i>DCu</i> | <i>DAl</i> | <i>TON</i> | <i>Si</i> | <i>PO4</i> | <i>O2</i> | <i>sal</i> | <i>Pot T</i> |
|----------|--------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|------------|-----------|------------|--------------|
| depth | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | |
| TDCo | 0.02 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | |
| TDMn | 0.02 | 0.62 | 1.00 | | | | | | | | | | | | | | | | | | | | | | |
| TDNi | 0.22 | 0.21 | -0.08 | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| TDCd | 0.34 | 0.06 | -0.02 | 0.32 | 1.00 | | | | | | | | | | | | | | | | | | | | |
| TDPb | 0.00 | 0.02 | -0.01 | 0.00 | 0.18 | 1.00 | | | | | | | | | | | | | | | | | | | |
| TDFe | 0.05 | 0.52 | 0.96 | -0.08 | 0.05 | 0.01 | 1.00 | | | | | | | | | | | | | | | | | | |
| TDZn | 0.27 | 0.06 | 0.04 | 0.24 | 0.44 | 0.15 | 0.08 | 1.00 | | | | | | | | | | | | | | | | | |
| TDCu | 0.37 | 0.24 | 0.31 | 0.38 | 0.39 | 0.03 | 0.31 | 0.37 | 1.00 | | | | | | | | | | | | | | | | |
| TDAI | 0.28 | 0.35 | 0.84 | -0.07 | 0.14 | 0.04 | 0.94 | 0.21 | 0.21 | 1.00 | | | | | | | | | | | | | | | |
| DCo | 0.10 | 0.50 | 0.00 | 0.22 | 0.27 | 0.16 | -0.03 | 0.07 | 0.09 | 0.07 | 1.00 | | | | | | | | | | | | | | |
| DMn | -0.06 | 0.46 | 0.73 | -0.14 | -0.07 | 0.05 | 0.71 | 0.00 | 0.26 | 0.42 | 0.24 | 1.00 | | | | | | | | | | | | | |
| DNi | 0.32 | 0.01 | -0.10 | 0.64 | 0.31 | -0.02 | -0.07 | 0.26 | 0.44 | -0.04 | -0.01 | -0.16 | 1.00 | | | | | | | | | | | | |
| DCd | 0.50 | 0.04 | 0.01 | 0.23 | 0.75 | 0.13 | 0.06 | 0.33 | 0.29 | 0.17 | 0.32 | 0.02 | 0.38 | 1.00 | | | | | | | | | | | |
| DPb | -0.07 | -0.24 | -0.45 | 0.15 | 0.40 | 0.13 | -0.35 | 0.19 | -0.09 | -0.35 | 0.17 | -0.34 | 0.29 | 0.46 | 1.00 | | | | | | | | | | |
| DFe | 0.16 | -0.11 | 0.01 | 0.00 | 0.03 | 0.01 | 0.16 | 0.03 | 0.11 | 0.22 | -0.09 | 0.11 | 0.05 | 0.06 | 0.07 | 1.00 | | | | | | | | | |
| DZn | 0.59 | 0.03 | -0.04 | 0.28 | 0.38 | 0.04 | 0.01 | 0.39 | 0.31 | 0.13 | 0.12 | -0.08 | 0.44 | 0.56 | 0.24 | 0.07 | 1.00 | | | | | | | | |
| DCu | 0.45 | 0.06 | 0.09 | 0.20 | 0.16 | 0.01 | 0.10 | 0.22 | 0.51 | 0.21 | 0.03 | 0.10 | 0.45 | 0.36 | 0.09 | 0.12 | 0.44 | 1.00 | | | | | | | |
| DAl | 0.77 | 0.06 | 0.27 | 0.06 | 0.44 | 0.03 | 0.34 | 0.26 | 0.35 | 0.50 | 0.17 | 0.11 | 0.15 | 0.53 | -0.19 | 0.04 | 0.54 | 0.40 | 1.00 | | | | | | |
| TON | 0.47 | -0.03 | -0.09 | 0.27 | 0.72 | 0.12 | -0.02 | 0.31 | 0.21 | 0.14 | 0.29 | -0.06 | 0.39 | 0.91 | 0.45 | 0.00 | 0.51 | 0.28 | 0.53 | 1.00 | | | | | |
| Si | 0.79 | 0.01 | -0.07 | 0.32 | 0.63 | 0.09 | -0.02 | 0.36 | 0.34 | 0.19 | 0.25 | -0.09 | 0.46 | 0.83 | 0.29 | 0.04 | 0.67 | 0.43 | 0.75 | 0.86 | 1.00 | | | | |
| PO4 | 0.48 | 0.02 | -0.08 | 0.26 | 0.78 | 0.13 | -0.03 | 0.42 | 0.26 | 0.15 | 0.29 | -0.07 | 0.39 | 0.90 | 0.46 | 0.00 | 0.58 | 0.42 | 0.51 | 0.95 | 0.86 | 1.00 | | | |
| oxygen | -0.05 | 0.21 | 0.08 | 0.17 | -0.14 | 0.01 | -0.04 | 0.01 | 0.31 | -0.07 | 0.11 | 0.15 | 0.20 | -0.28 | -0.14 | 0.01 | -0.10 | 0.21 | -0.23 | -0.32 | -0.23 | -0.25 | 1.00 | | |
| salinity | -0.21 | -0.14 | 0.02 | -0.24 | 0.10 | 0.03 | 0.09 | -0.03 | -0.46 | 0.02 | -0.02 | -0.02 | -0.32 | 0.12 | 0.10 | -0.01 | -0.15 | -0.51 | -0.08 | 0.20 | -0.06 | 0.14 | -0.57 | 1.00 | |
| Pot T | -0.78 | -0.13 | -0.01 | -0.35 | -0.56 | -0.09 | -0.03 | -0.34 | -0.55 | -0.21 | -0.31 | -0.03 | -0.52 | -0.75 | -0.20 | -0.12 | -0.64 | -0.63 | -0.65 | -0.69 | -0.84 | -0.72 | -0.19 | 0.41 | 1.00 |

Table S4. Atmospheric trace element total concentrations (pmol m⁻³) during spring and summer 2010. (Pb was not determined).

| | Al | Mn | Zn | Cu | Ni | Co | Cd |
|---------------|----------------|------------|----------|----------|-------|--------|----------|
| <i>Spring</i> | | | | | | | |
| TM02 | 1730±200 | 2.2±0.6 | <39 | 162±8 | <60 | <3.0 | 9.8±0.5 |
| TM03 | 2190±170 | 22.1±1.2 | <26 | 127±6 | <40 | <2.0 | 2.4±0.1 |
| TM04 | 1750±240 | 19.8±1.3 | 658±37 | 732±37 | <76 | <3.8 | 8.5±0.4 |
| TM05 | 9180±500 | 90.4±4.6 | <31 | 1070±50 | <47 | <2.3 | 10.4±0.5 |
| TM06 | 11500±650 | 114±6 | <52 | 108±5 | <80 | <4.0 | 4.3±0.2 |
| TM07 | 3660000±180000 | 34000±1700 | 3580±230 | 3730±190 | <620 | 357±18 | 176±9 |
| TM08 | 3000000±150000 | 29300±1460 | 2970±170 | 2550±130 | <380 | 275±14 | 90.9±4.5 |
| TM09 | 82900±5800 | 886±47 | <750 | <1060 | <2300 | <57 | <30 |
| <i>Summer</i> | | | | | | | |
| TM10 | 36±27 | 1.5±0.2 | 14.7±5.9 | <47 | <51 | <2.6 | <2.7 |
| TM11 | 1030±90 | 9.1±0.6 | 17.8±9.2 | <74 | <80 | <4.0 | <4.2 |
| TM12 | 298±42 | 1.4±0.3 | <12 | <53 | <57 | <2.9 | <3.0 |
| TM13 | 813±60 | 5.3±0.4 | 18.1±4.7 | <75 | <41 | <2.0 | <2.1 |
| TM14 | 597±44 | 2.3±0.2 | 7.3±3.3 | <27 | <29 | <1.5 | <1.5 |
| TM15 | 942±71 | 5.5±0.4 | <11 | <46 | <49 | <2.5 | <2.6 |

Table S5 - Major and trace element composition of ship-board collected ash samples. EYJ 04 ash sample was collected from atmospheric deposits onboard the RRS Discovery on May 8, 2010. EYJ07 was collected from Iceland at an earlier stage of the summit eruption (17/04/2010). JA-1 and JA-2 are Japanese Andesite standards used to determine the accuracy. RSD is the relative standard deviation of the measured standards. All major elements are presented in weight percentages (wt%) and trace elements in $\mu\text{g g}^{-1}$.

| Latitude | | N 63.1 | | N 63.5 |
|--------------------------------|-------|------------|--------|------------|
| Longitude | | W 18.5 | | W 19.6 |
| Date erupted | | 08/05/2010 | | 17/04/2010 |
| Samples | JA-1 | RSD (%) | EYJ 04 | EYJ 07 |
| Major and trace elements (XRF) | | | | |
| O | 46.2 | 0.55 | 45.6 | 45.1 |
| Si | 29.9 | 0.10 | 27.3 | 27.3 |
| Ti | 0.52 | 1.64 | 0.92 | 0.86 |
| Al | 7.93 | 1.12 | 7.91 | 7.77 |
| Fe | 5.4 | 1.21 | 7.59 | 7.62 |
| Mn | 0.12 | 3.22 | 0.17 | 0.18 |
| Mg | 0.97 | 1.78 | 1.83 | 1.48 |
| Ca | 4.06 | 0.25 | 3.81 | 3.35 |
| Na | 2.86 | 0.37 | 3.94 | 4.01 |
| K | 0.65 | 1.56 | 1.69 | 1.70 |
| P | 0.07 | 2.18 | 0.13 | 0.15 |
| Cr | 7 | 6.33 | 113.4 | 72.3 |
| Ni | 1.8 | 4.04 | 55.2 | 40.5 |
| Zn | 86.7 | 3.42 | 172.9 | 167 |
| V | 105 | 1.99 | 120.8 | 101.6 |
| Zr | 88.3 | 3.53 | 547 | 549 |
| Trace elements (ICP-MS) | | | | |
| | JA-2 | RSD (%) | | |
| Li | 29.28 | 0.44 | 14.1 | 15.0 |
| Sc | 18.0 | 1.63 | 15.6 | 14.6 |
| Rb | 72.4 | 1.35 | 42.7 | 43.5 |
| Sr | 243 | 1.92 | 284 | 289 |
| Y | 17.6 | 2.10 | 70.5 | 72.35 |
| Nb | 9.18 | 1.38 | 65.8 | 66.71 |
| Cs | 4.92 | 0.30 | 0.51 | 0.51 |
| Ba | 320 | 1.14 | 431 | 459 |

| | | | | |
|----|------|------|-------|-------|
| La | 16.0 | 0.26 | 52.87 | 55.56 |
| Ce | 33.6 | 0.27 | 119.7 | 126.1 |
| Pr | 3.78 | 1.49 | 14.8 | 15.8 |
| Nd | 14.4 | 0.94 | 60.1 | 64.6 |
| Sm | 3.13 | 0.59 | 13.5 | 14.5 |
| Eu | 0.90 | 0.67 | 3.83 | 4.38 |
| Gd | 3.03 | 0.66 | 13.4 | 14.2 |
| Tb | 0.48 | 0.04 | 2.11 | 2.24 |
| Dy | 2.91 | 0.32 | 12.5 | 13.1 |
| Ho | 0.59 | 2.29 | 2.44 | 2.55 |
| Er | 1.70 | 0.08 | 6.62 | 6.94 |
| Tm | 0.26 | 1.32 | 0.96 | 1.00 |
| Yb | 1.69 | 0.21 | 6.15 | 6.36 |
| Lu | 0.26 | 1.93 | 0.89 | 0.92 |
| Hf | 2.93 | 0.02 | 12.6 | 12.9 |
| Pb | 19.8 | 1.84 | 4.53 | 4.39 |
| Th | 4.90 | 1.49 | 5.97 | 6.19 |
| U | 2.23 | 0.83 | 1.91 | 1.95 |

Table S6. Fractional solubility (%) of trace elements during spring and summer 2010. (n.c. – solubility could not be calculated when both soluble and total concentrations were below detection limit. a – Lower limits are given when the total concentration was below detection limit, but the soluble concentration was not. b – contamination in soluble element measurement suspected, see Table S4).

| | Al | Mn | Zn ^a | Cu ^a | Ni ^a | Co ^a | Cd ^a |
|---------------|---------------------|---------------------|----------------------|-----------------|-----------------|-----------------|-----------------|
| <i>Spring</i> | | | | | | | |
| TM02 | 4.0±1.6 | 76±30 | >73 | 37.3±1.9 | >2 | n.c. | 135±7 |
| TM03 | 8.7±0.7 | 48±3 | >27 | 29.1±1.5 | n.c. | >4 | 99±6 |
| TM04 | 27.3±3.8 | 48±4 | 88±20 | 29.8±1.5 | >6 | >3 | 52±3 |
| TM05 | 4.6±0.3 | 12.8±0.9 | >57 | 39.7±2.0 | >2 | >5 | 39±2 |
| TM06 | 5.4±0.3 | 8.9±0.8 | >16 | 24.3±1.2 | >1 | >3 | 105±7 |
| TM07 | 0.92±0.05 | 0.96±0.06 | 5.4±0.9 | 3.9±0.2 | n.c. | 0.54±0.09 | 81±5 |
| TM08 | 0.59±0.03 | 0.86±0.05 | 2.1±0.7 | 11.4±0.6 | >1 | 0.72±0.07 | 81±5 |
| TM09 | 1.5±0.6 | 2.9±0.5 | n.c. | >14 | >0.4 | n.c. | >47 |
| <i>Summer</i> | | | | | | | |
| TM10 | 161±122 | 49±10 | 76±39 | >9 | >0.9 | >6 | >4 |
| TM11 | 8.8±1.2 | 27±3 | 138±78 | >15 | >2 | n.c. | >6 |
| TM12 | 182±26 | 112±23 | n.c. | >6 | >3 | n.c. | >3 |
| TM13 | 35.0±2.7 | 27±3 | 91±28 | >4 | >2 | >11 | >2 |
| TM14 | 360±30 ^b | 339±32 ^b | 415±195 ^b | >9 | >7 | >10 | >9 |
| TM15 | 13.5±1.1 | 27±3 | n.c. | >7 | >0.8 | n.c. | >4 |