Deep dissolved iron profiles in the eastern North Atlantic in relation to water masses

Agathe Laës, Stéphane Blain, Patrick Laan, Eric P. Achterberg, Géraldine Sarthou, H. J. W. de Baar

Deep dissolved iron profiles in the eastern North Atlantic in relation to water masses

A. Laës,[1] S. Blain,[1] P. Laan,[2] E. P. Achterberg,[3] G. Sarthou,[1] and H. J. W. de Baar[2]

[1]   Concentrations of dissolved iron (DFe, 0.2μm) were determined at two stations in the Biscay Abyssal Plain (North East Atlantic) in March 2002. DFe concentrations in the surface layer (0.23–0.34 nM) were typical of winter conditions in this area. At 1000 m, DFe concentrations increased to 0.62–0.86 nM. This feature is consistent with the production of DFe by remineralization of the biogenic material. However, at this depth, Mediterranean Outflow Water (MOW) could be an additional source of DFe. Below 2500 m, DFe concentrations were constant (0.75 ± 0.04 nM). An interesting feature of the profiles was the intermediate maximum of DFe (1.19–1.12 nM) around 2000 m, associated with the Labrador Sea Water (LSW). We suggest that the iron enrichment of LSW occurred when this water mass reached the continental margin, likely in the vicinity of the Goban plateau. Vertical distributions were highly dependent on water masses encountered.   INDEX TERMS: 4875 Oceanography: Biological and Chemical: Trace elements; 4283 Oceanography: General: Water masses; 4219 Oceanography: General: Continental shelf processes. **Citation:** Laës, A., S. Blain, P. Laan, E. P. Achterberg, G. Sarthou, and H. J. W. de Baar, Deep dissolved iron profiles in the eastern North Atlantic in relation to water masses, *Geophys. Res. Lett.*, *30*(17), 1902, doi:10.1029/2003GL017902, 2003.

1.   Introduction

[2]   Iron is one of the most abundant elements on earth [*Taylor*, 1964], nevertheless its concentrations in the ocean are mainly subnanomolar due to its low solubility. During the two past decades much attention has been paid to the determination of the concentrations of dissolved iron (DFe, 0.2 μm) in surface layers of the ocean, because low DFe concentrations can limit the growth of primary producers and consequently the transfer of CO_2 from the atmosphere to the ocean. By contrast, little work has been done to investigate the distribution of iron in intermediate and deep waters. Most of the profiles gathered in various oceanic basins exhibit a nutrient-like profile [*Johnson et al.*, 1997a]. Iron depletion in surface layers compared to deeper waters is not surprising, because iron is an essential nutrient actively removed from the surface layer by biological processes. Similarly to major nutrients, biogenic iron returns to the dissolved phase when biogenic material sinks and is

remineralized. These processes produce a smooth increase of DFe from the depth of the mixed layer until around 1000 m. At greater depth, DFe is apparently quite constant. In contrast to other major nutrients, no inter-basin fractionation has been clearly observed for iron. The factors controlling deep concentrations of DFe are not yet fully understood and are still actively debated [*Boyle*, 1997; *Johnson et al.*, 1997b; *Wu et al.*, 2001]. In addition to the ideal nutrient-like profiles described above, different anomalies have been reported. Dust deposition can significantly enhance the surface concentration of iron, leading to a maximum of DFe in surface waters [*Bruland et al.*, 1994; *Guieu et al.*, 2002]. Moreover, advection of a water mass influenced by a continental margin can also create anomalies in the intermediary section of the vertical profile [*de Baar et al.*, 1995; *Mackey et al.*, 2002]. We report here dissolved iron distribution for two deep stations, located close to the continental shelf in the Biscay Abyssal Plain. We examine the relationship between concentrations of dissolved iron and water mass distribution in this region.

2.   Sampling and Methods

[3]   Seawater samples were collected on board R/V *Pelagia* during the IRONAGES (Iron Resources and Oceanic Nutrients-Advancement of Global Environment Simulations) cruise (March 2002) following a transect from the shelf break in an offshore direction. The results presented here focus on two offshore stations: 27 (46°26′06″N, 06°59′79″W) and 28 (46°00′00″N, 8°00′00″W) (Figure 1).

[4]   Deep water sampling for nutrients and oxygen analysis, was performed using Niskin bottles attached to a rosette CTD frame. Surface samples were collected with the torpedo fish (see below). Winkler titration was performed to determine dissolved oxygen, whereas concentrations of nitrate were measured by segmented flow analysis.

[5]   Seawater samples for iron determination, were collected using GO-FLO bottles mounted on a Kevlar line. Surface waters (−3m) were sampled using a towed torpedo fish and a trace metal clean Teflon bellows pump. In both cases, seawater was filtrated through 0.2 μm cartridge (Sartobran) equipped with 0.45 μm prefilter and acidified to pH <2 with ultrapur HCl (Merck) for at least 24 hours before analysis. Flow Injection Analysis (FIA) with on line preconcentration and chemiluminescence detection was used for on board measurement of DFe concentration [*Obata et al.*, 1993]. The pH of the acidified sample was adjusted to 4.5 using ultrapure ammonia (Merck) and purified ammonium acetate buffer (2 M), before loading on the 8-hydroxyquinoline preconcentration column. Calibration curves were constructed using additions of known

[1]Laboratoire des sciences de l'environnement marin (LEMAR), Institut Universitaire Européen de la mer, Plouzané, France.
[2]Royal Netherlands Institute for Sea Research (NIOZ), Department of Marine Chemistry and Geology, Texel, The Netherlands.
[3]Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, United Kingdom.
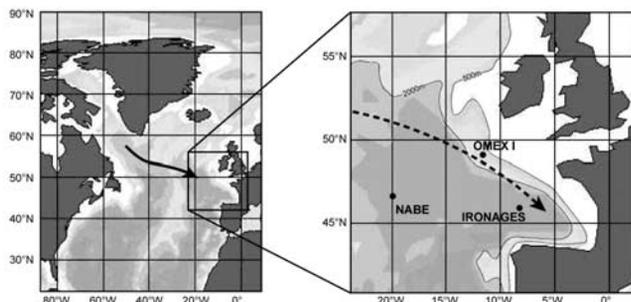
Figure 1. Map of the North Atlantic Ocean showing the South East extension of LSW, and sampling location for NABE, OMEX I and IRONAGES.

amount of dissolved iron to seawater with a DFe concentration below the detection limit. The mean limit of detection (3 times the standard deviation of 10 blank replicates) was 28 ± 28 pM (n = 14, one blank determination per day). The contribution of the FIA manifold to the blank was estimated using different times of preconcentration and extrapolating the signal to a preconcentration time equal to zero. The average blank was 39 ± 22 pM (n = 14). The contribution of the HCl, NH$_3$ and buffer addition to the blank was investigated by standard addition of each reagent in low iron seawater. Their contribution to the blank was below the limit of detection. The DFe concentrations were corrected from the total blank.

3. Results

3.1. Hydrology

[6] Water mass features in our study region are summarized in Table 1. Low Deep Water (LDW), characterized by low salinity and low temperature is found in the deepest part (>3000 m) of the water column. LDW contains high concentrations of silicic acid (37.62–46.78 μM), indicating the presence of Antarctic Bottom Water (AABW) [*van Aken*, 2000a]. Between 2300 and 3000 m, North Atlantic Deep Water (NADW) is identified. At approximately 2000 m, Labrador Sea Water (LSW) exhibits similar temperature and salinity signatures as NADW, but higher dissolved oxygen content. The characteristics of LSW in the Biscay Abyssal Plain are less well defined than at its source [*Pingree*, 1973]. LSW is overlapped by salty and low-oxygen Mediterranean Outflow Water (MOW). The upper layer (<700 m), is characterized by the surface waters and by the Eastern North Atlantic

Central Water (ENACW), formed in the North East Atlantic by deep winter time convection.

4. Discussion

4.1. Surface Waters

[7] The concentrations of DFe in surface waters (0.23 and 0.34 nM) at stations 27 and 28 (Figure 2), are of the same order of magnitude as those reported in the literature for the Northeast Atlantic. The lowest concentrations have been mentioned by [*Martin et al.*, 1993] (0.07–0.19 nM) at 47°N, 20°W, whereas [*de Jong et al.*, 2000] and [*Boye et al.*, 2003] reported much higher concentrations (0.80–1.50 nM) at 40°N, 23°W, and (0.71 ± 0.11 nM) at 45°N, 20°W, respectively. At the seasonal scale, biological activity greatly impacts the concentrations of nutrients and trace metals (e.g., Cd) in the euphotic layer of the studied region [*Cotté-Krief et al.*, 2002]. The relatively high nitrate concentrations measured during our cruise are typical of pre-bloom conditions in this area [*Tréguer et al.*, 1979]. Iron in the surface layer was probably not actively removed by phytoplankton at this time. Biological uptake may explain the difference from the lower DFe measured later in the season at the station 47 of the North Atlantic Bloom Experiment site (NABE) [*Martin et al.*, 1993] (Figure 1).

[8] However, variability in DFe concentrations during the same month [*de Jong et al.*, 2000], [*Boye et al.*, 2003] and our study, are more important than the differences between our stations and the NABE ones. This means that iron is probably not only influenced by seasonality. In fact, at mid latitudes, the Eastern North Atlantic ocean is highly dynamic. Strong currents and frontal zones create patchy surface distributions of nutrients. This may also be true for trace metals.

4.2. Mediterranean Outflow Water

[9] Salinity and oxygen signatures at 1000 m are typical of the Mediterranean Outflow Water (Figure 2). This water mass flows along the Portugal and Spain coast before reaching the Biscay Abyssal Plain at intermediate depth [*van Aken*, 2000b]. Generally, 1000 m is also the depth where concentrations of nutrients increase strongly due to remineralization of biogenic particles from the upper layers. Therefore it is not possible to firmly consider observed high concentrations of DFe (0.62 and 0.86 nM) as an inherent feature of MOW. Figure 3 shows DFe and apparent oxygen utilization (AOU) profiles at our stations and at St 47 (NABE) located westward (Figure 1). If we consider a remineralization ratio defined as the average concentration of DFe over the average AOU (for 3 depths around

Table 1. Properties of Water Masses at Stations 27 and 28

Water masses	Depth (m)	Salinity		Temperature (°C)		Dissolved oxygen (μM)		Dissolved iron (nM)	
		27	28	27	28	27	28	27	28
LDW	>3000	34.92	34.91	2.29	2.21	238.12	239.20	0.82	0.74
NADW	2300–3000	34.97	34.99	2.94	3.42	239.98	244.96	0.93	0.86
LSW	2000	34.99	35.02	3.60	4.01	251.75	254.39	1.19	1.12
MOW	1000	35.74	35.74	9.50	9.61	185.88	186.92	0.62	0.86
ENACW	700–50	35.55	35.56	11.04	11.06	214.10	199.53	0.60	0.77
Surface waters	50	35.60	35.64	12.31	12.57	262.81	258.57	0.23	0.34
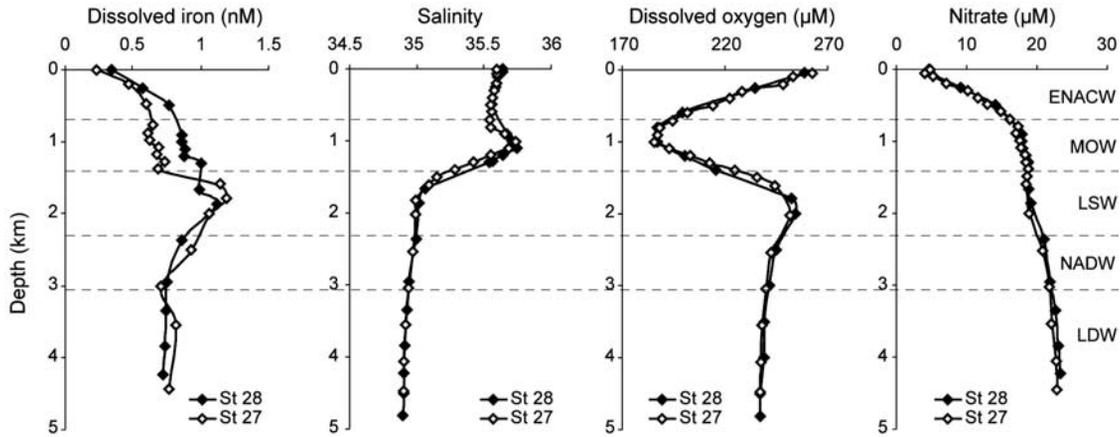
Figure 2. Concentrations of dissolved iron, salinity, dissolved oxygen, and nitrate, at stations 27 (46°26′06″N, 06°59′79″W) (open diamonds) and 28 (46°00′00″N, 08°00′00″W) (filled diamonds).

1000 m), we can compare the three stations. The ratios DFe/AOU for our study $6.64 \cdot 10^{-6}$ and $9.17 \cdot 10^{-6}$ are comparable with the one obtained for NABE: $6.31 \cdot 10^{-6}$. As the NABE station is not strongly influenced by MOW, our higher DFe concentrations obtained at 1000 m may be reasonably explained as a result of remineralization processes in the water column.

4.3. North Atlantic Deep Water and Low Deep Water

[10] At both stations, roughly constant concentrations of DFe (0.75 ± 0.04 nM; n = 7) were found below 3000 m (Figure 2). Such a constancy for DFe concentrations in deep waters has been noted previously [*Johnson et al.*, 1997a]. Our mean value is among the highest concentrations previously reported. Despite differences in analytical procedures which can complicate comparison between different data sets, slightly higher concentrations at our site are consistent with the proximity to the continental shelf environment, which constitutes a potential source of DFe.

4.4. Labrador Sea Water

[11] The different features of our iron profiles described in preceding sections are in good agreement with the

nutrient-type profile of DFe often observed in offshore waters. However, in our case, this type of profile is disturbed by an iron enriched plume observed around 2000 m (Figure 2). This anomaly was apparently not related to any special feature of the continental slope, which is mainly a very steep and rocky escarpment at our studied site. The high DFe signature fitted well with a minimum of salinity and a maximum of oxygen, whereas AOU was inversely related to DFe (Figure 3). During strong winter cooling, vertical mixing in the Labrador Sea generates LSW. Following deep convection, LSW travels from its source, through the Charlie Giffs Fracture across the North Atlantic Ocean, to finally extend along the Eastern shelf break [*Talley and McCartney*, 1982] (Figure 1). The AOU minimum (47.2 μmol/dm³) for station 47 sampled by *Martin et al.* [1993] showed the imprint of LSW at 2000 m. Although the vertical resolution of the DFe profile at these depths was poor, no maximum was observed. Very likely, the iron enrichment of LSW (1.19 and 1.12 nM) visible at our stations had its origin eastward, in the Southeast extension of LSW. After flowing through the Charlies Giffs Fracture, one part of LSW flows along the Northern Shelf boundary before entering the Biscay Abyssal Plain by the North.
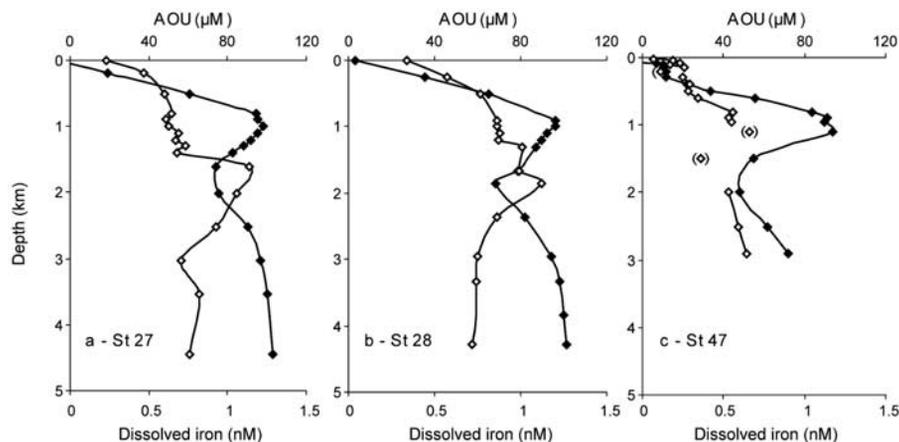
Figure 3. AOU (filled diamonds) and DFe (open diamonds) profiles at stations (a) 27, (46°26′06″N, 06°59′79″W), (b) 28 (46°00′00″N, 08°00′00″W), and station (c) 47 (47°00′00″N, 20°00′00″W) from [*Martin et al.*, 1993], (symbols in brackets are unpublished data, courtesy K. Johnson).

Anomalies of salinity suggest that the smooth topography of the Goban plateau is swept by LSW [*Paillet et al.*, 1998]. Moreover, during OMEX I (Ocean Margin EXchange), an intermediate nepheloid layer has been identified during winter time in this area [*McCave et al.*, 2001]. The base of this nepheloid layer extended down to 1600 m, exactly where LSW encounters MOW, which was flowing the opposite way [*Saunders*, 1982]. Lithogenic particles coming from the shelf are likely trapped along the density surfaces between the two water masses. Therefore the upper part of LSW may become DFe enriched while sweeping the boundary shelf, before entering the Biscay Abyssal Plain. This would also explain the DFe maxima observed slightly above the depth of the LSW core.

[12] Vertical distributions of DFe at our stations were highly related to water masses occurrence, as well as regenerative processes. In order to better understand the global iron cycling, we need to consider both the nutrient-type behavior of iron and the impact of the hydrography by the way of water masses advection, on iron distribution.

References

Boye, M., A. P. Aldrich, C. M. G. van den Berg, J. T. M. de Jong, M. Veldnuis, and H. J. W. de Baar, Horizontal gradient of the chemical speciation of iron in surface waters of the northeast Atlantic Ocean, *Mar. Chem.*, *80*, 129–143, 2003.

Boyle, E., What controls dissolved iron concentrations in the world ocean? A comment, *Mar. Chem.*, *57*, 163–167, 1997.

Bruland, K. W., K. J. Orians, and J. P. Cowen, Reactive trace metals in the stratified central North Pacific, *Geochim. Cosmochim. Acta*, *58 N°15*, 3171–3182, 1994.

Cotté-Krief, M.-H., A. J. Thomas, and J.-M. Martin, Trace metal (Cd, Cu, Ni and Pb) cycling in the upper water column near the shelf edge of the European continental margin (Celtic Sea), *Mar. Chem.*, *79*, 1–26, 2002.

de Baar, H. J. W., J. T. M. de Jong, D. C. E. Bakker, B. M. Löscher, C. Veth, U. Bathmann, and V. Smetacek, Importance of iron for plankton blooms and carbon dioxide drawdown in the Southern Ocean, *Nature*, *373*, 412–415, 1995.

de Jong, J. T. M., M. Boye, V. F. Schoemann, R. F. Nolting, and J. W. de Baar, Shipboard techniques based on flow injection analysis for measuring dissolved Fe, Mn and Al in seawater, *J. Environ. Monit.*, *2*, 496–502, 2000.

Guieu, C., Y. Bozec, S. Blain, C. Ridame, G. Sarthou, and N. Leblond, Impact of high Saharan dust inputs on iron concentrations in the Mediterranean Sea, *Geophys. Res. Lett.*, *29*(19), 1911, doi:10.1029/2001GL014454, 2002.

Johnson, K. S., R. M. Gordon, and K. H. Coale, What controls dissolved iron concentrations in the world ocean?, *Mar. Chem.*, *57*, 137–161, 1997a.

Johnson, K. S., R. M. Gordon, and K. H. Coale, What controls dissolved iron concentrations in the world ocean? Authors' closing comments, *Mar. Chem.*, *57*, 181–186, 1997b.

Mackey, D. J., J. E. O'Sullivan, and R. J. Watson, Iron in the western Pacific: A riverine or hydrothermal source for iron in the Equatorial undercurrent?, *Deep Sea Res. Part I*, *49*, 877–893, 2002.

Martin, J. H., S. E. Fitzwater, R. M. Gordon, C. N. Hunter, and S. J. Tanner, Iron, primary production and carbon-nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment, *Deep Sea Res. Part II*, *40*, 115–134, 1993.

McCave, I. N., I. R. Hall, A. N. Antia, L. Chou, F. Dehairs, R. S. Lampitt, L. Thomsen, T. C. E. van Weering, and R. Wollast, Distribution, composition and flux of particulate material over the European margin at 47°–50°N, *Deep Sea Res. Part II*, *48*, 3107–3139, 2001.

Obata, H., H. Karatani, and E. Nakayama, Automated determination of iron in seawater by chelating resin concentration and chemiluminescence detection, *Anal. Chem.*, *65*, 1524–1528, 1993.

Paillet, J., M. Arhan, and M. S. McCartney, Spreading of Labrador Sea Water in the eastern North Atlantic, *J. Geophys. Res.*, *103*, 10,223–10,239, 1998.

Pingree, R. D., A component of Labrador Sea Water in the Bay of Biscay, *Limnol. Oceanogr.*, *18*(5), 711–718, 1973.

Saunders, P. M., Circulation in the eastern North Atlantic, *J. Mar. Res.*, *40*, 641–657, 1982.

Talley, L. D., and M. S. McCartney, Distribution and circulation of Labrador Sea Water, *J. Phys. Oceanogr.*, *12*, 1189–1205, 1982.

Taylor, S. R., Abundance of chemical elements in the continental crust: A new table, *Geochim. Cosmochim. Acta.*, *28*, 1273–1285, 1964.

Tréguer, P., P. Le Corre, and J. R. Grall, The seasonal variations of nutrients in the upper waters of the Bay of Biscay region and their relation to phytoplankton growth, *Deep Sea Res.*, *26A*, 1121–1152, 1979.

van Aken, H. M., The hydrography of the mid-latitude northeast Atlantic Ocean I: The deep water masses, *Deep Sea Res. Part I*, *47*, 757–788, 2000a.

van Aken, H. M., The hydrography of the mid-latitude Northeast Atlantic Ocean II: The intermediate water masses, *Deep Sea Res. Part I*, *47*, 789–824, 2000b.

Wu, J., E. Boyle, W. Sunda, and L.-S. Wen, Soluble and colloidal iron in the oligotrophic North Atlantic and North Pacific, *Science*, *293*, 847–849, 2001.

————————————

A. Laës, S. Blain, and G. Sarthou, Laboratoire des sciences de l'environnement marin (LEMAR), Institut Universitaire Européen de la mer, Plouzané, France. (agathe.laes.@univ-brest.fr)

P. Laan and H. J. W. de Baar, Royal Netherlands Institute for Sea Research (NIOZ), Department of Marine Chemistry and Geology, Texel, The Netherlands.

E. P. Achterberg, Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, United Kingdom.