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Labile Fe(II) concentrations in the Atlantic sector of the Southern Ocean along a transect from the subtropical domain to the Weddell Sea Gyre

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Abstract

Labile Fe(II) distributions were investigated in the Sub-Tropical South Atlantic and the Southern Ocean during the BONUS-GoodHope cruise from 34 to 57° S (February–March 2008). Concentrations ranged from below the detection limit (0.009 nM) to val-

- ⁵ ues as high as 0.125 nM. In the surface mixed layer, labile Fe(II) concentrations were always higher than the detection limit, with values higher than 0.060 nM south of 47° S, representing between 39% and 63% of dissolved Fe (DFe). Biological production was evidenced. At intermediate depth, local maxima were observed, with the highest values in the Sub-Tropical domain at around 200 m, and represented more than 70% of
- ¹⁰ DFe. Remineralization processes were likely responsible for those sub-surface maxima. Below 1500 m, concentrations were close to or below the detection limit, except at two stations (at the vicinity of the Agulhas ridge and in the north of the Weddell Sea Gyre) where values remained as high as ~0.030–0.050 nM. Hydrothermal or sediment inputs may provide Fe(II) to these deep waters. Fe(II) half life times ($t_{1/2}$) at 4 °C
- ¹⁵ were measured in the upper and deep waters and ranged from 2.9 to 11.3 min, and from 10.0 to 72.3 min, respectively. Measured values compared quite well in the upper waters with theoretical values from two published models, but not in the deep waters. This may be due to the lack of knowledge for some parameters in the models and/or to organic complexation of Fe(II) that impact its oxidation rates. This study helped to
 ²⁰ considerably increase the Fe(II) data set in the Ocean and to better understand the Fe redox cycle.

1 Introduction

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Iron (Fe) is an essential micronutrient for all marine organisms, playing a key role in many metabolic processes, such as photosynthesis, respiration, nitrate reduction, and nitrogen fixation (Sunda, 1988, 1989). Its low concentrations have been shown to limit primary production in more than 50% of the ocean (Boyd and Ellwood, 2010). All



natural and artificial Fe fertilization experiments unequivocally showed the importance of Fe for the carbon cycle, particularly for the growth and composition of the phytoplanktonic community (Boyd et al., 2000; Coale et al., 1996; Gervais et al., 2002; Tsuda et al., 2003; Boyd, 2004; Coale et al., 2004; Blain et al., 2007; Pollard et al., 2007). De-5 spite numerous studies on Fe cycling the last 25 years, lots of unknowns persist, in particular because Fe chemistry in seawater is very complex. Fe has been observed to occur in two redox states (Fe(III) and Fe(II), Waite and Morel, 1984). In oxic seawater, the thermodynamically most stable state is Fe(III), but is highly insoluble (0.011 nM in 0.7 NaCl solution, Liu and Millero, 2002) and is rapidly hydrolyzed resulting in the formation of various Fe(III) oxyhydroxide (de Baar and de Jong, 2001). These species, 10 with $Fe(OH)_3$ being the dominant one in seawater at pH ~8, have the tendency to form colloidal Fe (Kuma et al., 1996) which coagulate and form particulate Fe (Johnson et al., 1997). In contrast to Fe(III), Fe(II) is more soluble but is rapidly oxidized by oxygen (O_2) and hydrogen peroxide (H_2O_2) (Millero et al., 1987; Millero and Sotolongo, 1989; 15 Santana-Casiano et al., 2004, 2005; Gonzalez-Davila et al., 2005, 2006). Although

- Fe(II) in seawater is less stable than Fe(III), recent models of Fe acquisition by eukaryotic phytoplankton suggest that the reduction of Fe(III) to Fe(II), with subsequent re-oxidation to Fe(III), is a possible mechanism by which Fe is made more bioavailable to phytoplankton (Shaked et al., 2004; Salmon et al., 2006; Maldonado et al., 2006; Morel et al., 2008). Numerous studies have investigated the oxidation of Fe(III) by O
- ²⁰ Morel et al., 2008). Numerous studies have investigated the oxidation of Fe(II) by O_2 and H_2O_2 in different aqueous solutions to understand the behavior of Fe(II) in natural waters (Santana-Casiano et al., 2006 and references herein). The most widely accepted mechanism to describe Fe oxidation with O_2 and H_2O_2 is the Haber-Weiss mechanism, with reactions 1 or 3 limiting the overall oxidation rate (King et al., 1995).

Fe(II) +
$$O_2 \rightarrow Fe(III) + O_2^{\bullet-}$$

$$2\mathsf{H}^{+}+\mathsf{Fe}(\mathsf{II})+\mathsf{O}_{2}^{\bullet-}\rightarrow\mathsf{Fe}(\mathsf{III})+\mathsf{H}_{2}\mathsf{O}_{2}$$

 $Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^{\bullet}$

(1)

(2)

(3)

 $Fe(II) + HO^{\bullet} \rightarrow Fe(III) + OH^{-}$

(4)

The rates for Eq. (1–4) strongly depend on the relative concentrations of the individual Fe(II) species in solution, mainly Fe^{2+} , $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2$, FeHCO_3^+ , $\text{Fe}(\text{CO}_3)_2^{2-}$, and $\text{Fe}\text{CO}_3(\text{OH}^-)$ (Millero, 1989; King, 1998; Santana-Casiano et al., 2006; Trapp and

- ⁵ Millero, 2007), as well as on the concentrations of O_2 and H_2O_2 , pH, temperature (*T*) and salinity (*S*). In warm oxygenated seawater, the half-life of Fe(II) can be as low as few seconds (King, 1998), whereas in cold surface or suboxic waters it can be on the order of hours to days (Croot et al., 2001, 2008; Hansard et al., 2009; Moffett et al., 2007).
- Several mechanisms provide Fe(II) in the dissolved phase and are reviewed by Hansard et al., 2009). They consist of in-situ processes (both abiotic and biotic) and external sources. The abiotic in-situ processes are mainly photochemical reactions. They include photoreduction of dissolved Fe(III) (oxy)hydroxides, and photoreduction or photolysis of organic, colloidal and particulate Fe (Rich and Morel, 1990; Wells et
- al., 1991; Kuma et al., 1992a, b; King et al., 1993; Barbeau et al., 2001; Rijkenberg et al., 2006). Extracellular reduction of Fe(III) by photochemically-produced superoxide or reductive dissolution of particulate Fe(III) may also occur (Voelker and Sedlak, 1995; Rose and Waite, 2002, 2003; Kustka et al., 2005; Rose et al., 2005; Salmon et al., 2006). Biotic in-situ processes include bioreduction of organic Fe(III) at cell surface
- (Maldonado and Price, 2001, 1999; Shaked et al., 2004; Morel et al., 2008), reduction by biogenic superoxide (Rose and Waite, 2002, 2003; Salmon et al., 2006), as well as remineralization via microbial activity (Alldredge and Cohen, 1987), cell lysis (Gobler et al., 2002), and grazing (Hutchins and Bruland, 1994; Hutchins et al., 1995; Sarthou et al., 2008). The external sources are atmospheric inputs (Kieber et al., 2001; Salmon et al., 2001; Salmon et al., 2008).
- Journet et al., 2007; Ozsoy and Saydam, 2001), sediment inputs (Elrod et al., 2004; Lohan and Bruland, 2008), submarine groundwater discharge (Windom et al., 2006), and hydrothermal vents (Coale et al., 1991; Chin et al., 1994; Field and Sherrell, 2000; Statham et al., 2005; Bennett et al., 2008). These sources supply Fe(II), which can then be transported by advective and/or diffusive mixing.



Although it is now evident that Fe(II) plays a key role in Fe chemistry and bioavailability in the ocean, there are relatively few open-ocean measurements of Fe(II) available due to the difficulty to measure such an ephemeral species at subnanomolar concentrations (Bruland and Rue, 2001). To our knowledge, the most comprehensive data set of Fe(II) was published by Hansard et al. (2009) in the Pacific Ocean along a zonal transect at 30° N and a meridional one at 152° W, within the CLIVAR/CO₂ Repeat Hydrography Program. In this paper, we present results of the Bonus-GoodHope (BGH) cruise, carried out in February-March 2008 during the International Polar Year in the Sub-Tropical South Atlantic and the Southern Ocean. Fe(II) distributions as well as oxidation rates are presented and results are discussed considering different processes such as photoreduction, oxidation, biological production, and different inputs, such atmospheric, sediment, and hydrothermal inputs, and/or advection and mixing.

2 Materials and methods

2.1 Study area

¹⁵ Sampling and ship board measurements were done aboard *R/V* Marion Dufresne from 8 February to 24 March 2008 in the Atlantic sector of the Southern Ocean during the BGH cruise. Figure 1 shows the cruise track together with the main oceanographic fronts and domains crossed during the cruise, from north to south: (i) the subtropical domain and the southern subtropical front (S-STF), (ii) the Antarctic Circumpolar Current (ACC) domain with 3 fronts crossed, the subantarctic front (SAF), the polar front (PF) and the southern ACC front (SACCF), and (iii) the eastern part of the Weddell Sea gyre with the southern boundary (SBdy) separating this domain from the ACC. Twelve stations were sampled for Fe(II), among which seven were sampled between 0 and 2000 m (Large stations L1 to L7) and five between 0 to 4000 m (Super stations S1 to S5). The position of each station is reported in Fig. 1 and Table 1.



2.2 Sample processing and analytical methods

Samples were collected using acid-cleaned 12 L Go-Flo bottles. When not in use, the Go-Flo bottles were stored inside a clean van with plastic bags covering the top and the bottom including the spigots. On station, the Go-Flo bottles were transferred to
the sampling deck and mounted on a Kevlar cable. Plastic bags were removed just after attachment to the Kevlar cable. When the expected depths were reached, bottles were tripped by a Teflon® messenger. Once back on board, the bottles were directly transferred to the clean van for sub-sampling. All sub-samples for Fe(II) measurements were immediately collected in previously 60 mL acid-cleaned high density brown polyethylene (HDPE) bottles. The maximum time between sub-sampling time from the Go-Flo bottle and analysis was 3 min. In order to minimize this time, no filtration was carried out, thus avoiding an underestimation of Fe(II) concentrations due to rapid oxidation. However, Fe(II) produced by fast-kinetic processes involving lithogenic or biogenic particles, such as reductive dissolution of particulate Fe(III) (Rich and Morel.

- 15 1990) or bioreduction of organic Fe(III) at cell surface (Maldonado and Price, 1999, 2001; Shaked et al., 2004; Morel et al., 2008) is measured and tends to overestimate Fe(II) concentrations. On the other hand, filtration step can also bring some artifacts. A first one is the damage and explosion of the cells that may release Fe(II) in the dissolved phase (Hutchins et al., 1993). A second one is related to the stress of the cells
- ²⁰ during filtration that may increase the production of superoxide (Godrant et al., 2009). This reactive oxygen species is involved in the redox Fe cycle, but it also initiates the three-step oxidation of luminol (Ussher et al., 2005; Rose and Waite, 2001), thus potentially inducing an overestimation of the Fe(II) concentrations in the dissolved phase. In the following, the term "labile" Fe(II) is then used, since the measurement is opera-²⁵ tionally defined and the exact speciation of the measured fraction is not known (Ussher
- et al., 2007).

Labile Fe(II) concentrations were determined by chemiluminescence flow injection analysis following the method of Croot and Laan (2002). As in Croot and Laan (2002),



there was no preconcentration prior to reaction with luminol, allowing a minimal analytical time (\sim 80–90 s). The percentage of labile Fe(II) was calculated as the ratio of labile Fe(II) over the dissolved Fe concentration (i.e. (Fe(II)/DFe) \cdot 100). The instrument was calibrated by standard addition using peak height measurements and freshly prepared

- acidified Fe(II) standards added to a surface (20–300 m) and a deep (500–2000 m) sample. Samples were stored at 4°C in the dark for 24 h to enable complete decay of ambient Fe(II). Non-linear calibration curves were observed, due to the kinetics of luminol oxidation and free-radical generation (Rose and Waite, 2001), and a polynomial 2nd degree curve-fitting technique was used to quantify the results. The blank was
 determined by running an aged seawater sample (4°C for 24 h). The detection limit
- was calculated as three times the standard deviation of the blank value and was equal to 0.009 ± 0.006 nM (n = 29).

After each Fe(II) spike, the change in Fe(II) signal was recorded over 10 min every 80–90 s, and allowed us to estimate Fe(II) oxidation rates, similarly to Roy et al (2008).
The oxidation rates may be overestimated by up to ~10% due to pH decrease after standard addition (~0.1 pH unit/standard addition). In addition to the samples used for the calibrations, for the four super stations S2 to S5, analyses were also performed with deeper samples (2300–3600 m).

2.3 Ancillary measurements

- Samples for dissolved Fe (Fe(III) + Fe(II), DFe) and hydrogen peroxide (H₂O₂) analyses were collected from the same Go-Flo bottles as for labile Fe(II) measurements in acid-washed low density polyethylene (LDPE) and high density brown polyethylene (HDPE) bottles, respectively. DFe concentrations were determined by FIA with on line preconcentration onto 8-HQ resin and chemiluminescence detection (Obata et al.,
- ²⁵ 1993; modified by Sarthou et al., 2003). The comprehensive data set is published elsewhere (Chever et al., 2010). H₂O₂ samples were analyzed on board within 3 h after collection using a flow injection method with chemiluminescent detection (Yuan and Shiller, 1999). A comprehensive data set will be available elsewhere (Bucciarelli



et al., 2011). The other ancillary parameters were measured from the closest (15–50 min) CTD cast. In-situ *T* and *S* were acquired from a CTD SEABIRD SBE 911+ mounted in a Niskin-rosette. Oxygen (O_2) concentrations were measured on board by Winkler titration. The pH was measured in total scale at a constant temperature of

⁵ 25 °C (pH_{*T*,25}) using an automated spectrophotometric technique with m-cresol purple as indicator (Gonzalez-Dávila et al., 2003). A VINDTA 3C system (Mintrop et al., 2000), with coulometer determination was used for the titration of the total dissolved inorganic carbon (C_T) after phosphoric acid addition. Carbonate concentration were estimated from pH_{*T*,25}, total alkalinity (potentiometrically titrated, Mintrop et al., 2000) and C_T , and computed by using CO2sys.xls v12 (Lewis and Wallace, 1998).

3 Results

3.1 Hydrography

The hydrography of the area is detailed in Chever et al. (2010), based on Gladyshev et al. (2008) and using the *S* and *T* data measured during the BGH cruise (Fig. 2).
The subtropical domain (STZ) extended southward to the S-STF (about 42° S, between station L2 and S2). Although station S2 is located south of the S-STF, its surface waters exhibit *S* and *T* signatures of subtropical waters. This station will be considered in the following as a Sub-Tropical station. Further south, the domain of the ACC extended to the Southern Boundary (SBdy) (~42° S to ~55° S, stations S2 to L7). The SAF, PF and SACCF were found at ~44° S, 50° S, and 51° S, respectively. South of the Sbdy (station S5), waters were entrained in the large scale cyclonic flow of the Weddell gyre.

Along the transect, several major water masses were sampled. They are described elsewhere (Arhan et al., 2011; Speich et al., 2011) and briefly summarized here and on Fig. 2. In the subtropical domain, the central water layer was mostly occupied by waters of Indian Ocean origin (Boebel et al., 2003). Below, the Antarctic Intermediate Water (AAIW), the Upper Circumpolar Deep Water (UCDW), the diluted North Atlantic Deep



Water (NADW), and finally the Antarctic Bottom Water (AABW) were observed. In the ACC, between the SAF and PF, below the surface mixed layer (SML) were located the AAIW, the Winter Waters (AAWW, marked by a T minimum), the UCDW, and the Lower Circumpolar Deep Water (LCDW) with, north of the PF, an addition of diluted South

- ⁵ West NADW (SW-NADW, Whitworth III and Nowlin, 1987). Deeper, the AABW was observed against the northern flank of the Mid Atlantic Ridge (MAR). Finally, south of the SBdy, the near surface waters were thought to have been in contact with the western continental margin of the Antarctic Peninsula, while the deeper waters might have had a more recent contact with the northern topographic limit of the Weddell Basin (Orri et al., 1992; Meredith et al., 2000; Klatt et al., 2005).
- ¹⁰ (Orsi et al., 1993; Meredith et al., 2000; Klatt et al., 2005).

3.2 Labile Fe(II) concentrations

Labile Fe(II) concentrations are reported in Table 2 and plotted on Fig. 3a. Within the whole data set, concentrations ranged from values below the detection limit to values as high as 0.125 nM.

- ¹⁵ In the SML, labile Fe(II) concentrations were systematically higher than the detection limit. Over the whole transect, the mean value was equal to 0.039 ± 0.024 nM (n = 26, median value = 0.037) and concentrations ranged from 0.012 nM to 0.116 nM. Both the minimum and maximum values were observed in the ACC (Station L7, 60 m, and station S4, 30 m, respectively). The highest percentages of Fe(II) relative to DFe (40–67%,
- Fig. 3b) were found at three stations south of 47° S (S3, S4, and S5) and were associated with values of Fe(II) higher than 0.060 nM. At the other stations, percentages were lower, ranging from 3% to 25%.

At intermediate depth (between the SML and 1500 m), values ranged from below the detection limit to 0.125 nM (Station S2, 196 m). The maxima observed around 200–300 m, more pronounced in the sub-tropical zone, corresponded to percentages

25 200–300 m, more pronounced in the sub-tropical zone, corresponded to percentages of labile Fe(II) relative to DFe ranging from 30% to 70%. Elsewhere values varied between less than 1% and 26%.



Below 1500 m, except at station S2 where values were around 0.030 nM at ~2000 m and at station S5 where values ranged from 0.035 to 0.050 nM below 2100 m, labile Fe(II) concentrations were close to or below the detection limit (mean value 0.010 ± 0.002 nM, n = 11), representing less than 4% of DFe.

5 3.3 Fe(II) oxidation rates

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The natural logarithm transformation of Fe(II) chemiluminescence over time showed linear decreases in signal for all surface and deep samples and spike additions, indicating a pseudo first-order kinetics for Fe(II) oxidation during the timescale monitored (Fig. 4). The pseudo-first order rate constants k_{ox} at 4°C were experimentally determined as the slope of the In-transformed chemiluminescence signal vs. time. The half-lifes ($t_{1/2}$) were then calculated as $t_{1/2} = \ln(2)/k_{ox}$, for the four Fe(II) spikes (Fig. 5, Table 3).

In the upper waters (20–300 m), values ranged from 2.9 to 11.3 min and increased significantly with latitude (linear regression, $r^2 = 0.65$, slope = 0.3 min/° S, P < 0.01,

- ¹⁵ n = 12). The mean value of all data was equal to 6.7 ± 2.6 min (median value 6.7 min). In the deep waters (500–2000 m), $t_{1/2}$ varied between 10.0 and 72.3 min. No significant relationship was observed with latitude (linear regression, P = 0.57). The mean value of all the data at depth was equal to 37.0 ± 19.7 min (median value 35.2 min). On average, $t_{1/2}$ was 6 times higher in the deep than in the upper waters. At the four super stations where two different depths were sampled below 500 m, values were not
- significantly different (paired t-test, P = 0.6, n = 4).



4 Discussion

4.1 Comparison with previously reported Fe(II) data

There are relatively few Fe(II) data reported in the literature (Table 4). Previous studies have been either generally geographically restricted, except the one carried out

⁵ by Hansard et al. (2009), or focused on particular areas, such as the suboxic zones, or performed during artificial Fe experiments in the Southern Ocean or the Subarctic Pacific.

For the open ocean, measurements were done in the Pacific Ocean (Hansard et al., 2009; O'Sullivan et al., 1991), the Atlantic Ocean (Bowie et al., 2002; Boye et al., 2003, 2006), and the Southern Ocean (Croot et al., 2007). Typically, Fe(II) concentrations range from the detection limit to ~0.050–0.080 nM, with concentrations that tend to increase in the surface waters due to photoproduction processes or in water masses influenced by continental margins. Indeed, studies carried out in continental or shelf waters showed concentrations up to 0.3–0.5 nM (Boye et al., 2006; Hansard et al.,

- ¹⁵ 2009), and even 3 nM (Waite et al., 1995). These high concentrations were likely due to transport of sediment-derived Fe and/or diffusion of Fe(II) directly from pore waters. These processes were even more pronounced in Fe-rich coastal environments, where values of Fe(II) could reach 40 nM (Hong and Kester, 1986). In suboxic zones, low oxygen concentrations slow down the oxidation rates of Fe(II) and maxima of Fe(II) (0.2–
- 0.6 nM) were associated with the oxygen minima and/or nitrite maxima (Hopkison and Barbeau, 2007; Moffett et al., 2007). During the artificial Fe fertilization experiments, concentrations of Fe(II) were shown to remain elevated (>0.2 nM and up to 1 nM) for several days after enrichment (Croot et al., 2001, 2005, 2008; Croot and Laan, 2002), due to a potential combination of slow oxidation rate and organic complexation (Roy et al., 2008).

Our values are within the range of variation of values in the open ocean and/or suboxic regions, although most of the previous studies measured Fe(II) in the dissolved phase. As already mention in Sect. 2.2, the non filtration may induce underestimation



or overestimation of the Fe(II) signal, but the good consistency between our data set and previous one suggests that it may be a non-issue. Another difference in methodology is the acidification of the samples at pH 6 prior to analysis (Hansard et al., 2009) to reduce the rate of Fe(II) oxidation. Although the acidification step may result in a measurement of "readily reducible Fe(III)" rather than actual Fe(II), the similarity between the two data set suggests that the method of Hansard et al. (2009) adequately corrected for apparent Fe(III) reduction caused by acidification.

4.2 Spatial and vertical distribution of labile Fe(II) during the BGH cruise

On the contrary to DFe concentrations (Chever et al., 2010), no systematic decrease in labile Fe(II) concentrations was observed from the north to the south of the section. The high values of DFe in the STZ were suggested to be due to direct dust deposition coming from Patagonia and/or to lateral advection of Indian Ocean water masses enriched by dust inputs. Another potential source of DFe was the African continental margin both in the SML and deeper waters (Chever et al., 2010). The mean advective time of these waters estimated from the AVISO Mean Absolute Dynamic Topography 15 (Ducet et al., 2000) for both the specific cruise period (2007-2008) and for the entire satellite time series (i.e., from 1992 to 2008) was equal to 1–3 months. Given the very short half-life time of Fe(II) in surface and deep waters (3-72 min), this delay is likely to be too long to preserve the signal of a potential enrichment of water masses by the African continental margin, unless stabilization of Fe(II) by organic complexation 20 occurs (Roy et al., 2008). In the following, we will examine more in detail the depth profiles of labile Fe(II) and discuss the potential sources of Fe(II) in our studied area.

4.2.1 Surface mixed layer (SML)

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Variations in Fe redox speciation along the day in the SML have been observed in numerous studies (e.g. Hong and Kester, 1986; Johnson et al., 1994; O'Sullivan et al., 1991; Waite et al., 1995; Bowie et al., 2002; Roy et al., 2008). In our study, 5 stations were sampled at night (S1, L2, L4, L6 and L7) and 7 during the day (L1, S2, L3,



- S3, L5, S4 and S5). The daytime and nighttime mean values were not significantly different (0.044±0.029 nM and 0.033±0.012 nM, respectively, student test, P = 0.39). Unexpectedly, daytime values were negatively correlated to the SML-integrated solar radiation (ANOVA, F = 9.12, P < 0.01). A parameter that appeared to control the labile Fe(II) values in our data set was the time at which samples were taken. Indeed,
- maximum values of labile Fe(II) as well as %Fe(II)/DFe were observed for the three stations (S3, S4 and S5) sampled between 12:00 and 16:00 (Universal Time, Fig. 6). This is consistent with photochemical reactions producing Fe(II) in the SML (Rich and Morel, 1990; Wells et al., 1991; Kuma et al., 1992a, b; King et al., 1993; Barbeau et al.,

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- ¹⁰ 2001; Rijkenberg et al., 2006; Voelker and Sedlak, 1995; Rose and Waite, 2002, 2003; Kustka et al., 2005; Rose et al., 2005; Roy et al., 2008). However, at these stations, the time between the tripping of the Go-Flo bottles (removing the sample from the influence of light) and analysis (15–20 min) were higher than the measured half-life times of Fe(II) (9–11 min). When estimating the initial in situ values that Fe(II) would have if
- photochemical reactions were the only sources of Fe(II), values are ~2-fold the DFe concentrations. This would suggest that photochemical reactions could not be the only sources of Fe(II) and that a biological production occurred. This would be coherent with a higher photosynthetic efficiency around noon (Legendre et al., 1988). Moreover, the biological superoxide production rates have been recently measured in oceanic
- ²⁰ and coastal waters of the Gulf of Alaska and values were up to 0.3 nM min⁻¹ (Hansard et al., 2010). Considering our labile Fe(II) data and measured $t_{1/2}$, and assuming steady-state, the calculated Fe(II) production rate was about 0.002–0.013 nM min⁻¹. The potential production rates of superoxide were thus likely sufficient to drive Fe(II) production. If a biological production exists in the surface waters, that would explain
- ²⁵ our values higher than the detection limit even at stations sampled at night. This night time observation of Fe(II) at pM levels was already done during the FeCycle experiment in the HNLC waters of the South West Pacific (Croot et al., 2007). These authors estimated that ~26% of the inorganic Fe(II) biologically produced would be organically complexed and the rest would be oxidized.



During the ANT XXIV/3 cruise, maxima of DFe and dissolved manganese (Mn) were observed in the surface waters in the Bouvet region at 54-55° S (Klunder et al., 2010; Middag et al., 2010), and were ascribed to recent deposition of aeolian dust originating from South America. At our L7 station (~55°S), however, no surface maximum of labile Fe(II) was observed, neither clear surface maxima of DFe in the Bouvet region 5 (Chever et al., 2010). This may be due to the fact that our sampling was performed three weeks later than theirs and/or to our lower sampling resolution, missing some of the key features they observed in the Bouvet region. At station S4 (~52° S), where we observed the highest value of labile Fe(II) in the SML, a combination of atmospheric inputs, biological production and photochemical processes (see above) might explain this high value.

4.2.2 Intermediate depths (between the SML and 1500 m)

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In the STZ (stations L1, S1, L2, and S2), large sub-surface maxima of labile Fe(II) centered at 200-300 m were observed. Concentrations started to increase just at or below the maximum of chlorophyll-a (Ras and Clautres, pers. com.) and high val-15 ues were observed as deep as 700 m (0.09 nM, station S1). Although generally lower than in the STZ (0.023–0.087 nM), sub-surface maxima were also observed in the ACC and north of the Weddell Gyre at depth between 60 and 300 m. As discussed above, due to the relatively long transport time between the African continental margin and the stations in the STZ, an input of Fe(II) from water masses enriched by the African 20

- continental margin is unlikely, unless organic complexation stabilized Fe(II) (Roy et al., 2008). Observed trends in labile Fe(II) compare well with depth profiles of dissolved Mn in the same sector of the Southern Ocean during the ANT XXIV/3 expedition (Middag et al., 2010). Sub-surface maxima of Mn were identified at depth around 150 m and coincided with a gradient in the potential density anomaly (σ_{θ}). Similar relationship
- 25 was evidenced for ²³⁴Th/²³⁸U ratio in the subsurface, with a steep increase towards values near or over 1 at the pycnocline (Rutgers van der Loeff et al., 2011). This trend in ²³⁴Th/²³⁸U ratio indicates no more scavenging of biogenic particles at the base of



the mixed layer and may rely on small scale remineralisation of sinking material (Cai et al., 2008, Maiti et al., 2010). During the BGH cruise, high resolution depth profiles were also obtained for ²³⁴Th/²³⁸U ratio and a more detailed data set is available from the surface to 1000 m depth (Planchon et al., 2011). Except at station L6, our labile Fe(II) maxima also coincided with increases in ²³⁴Th/²³⁸U ratios in the subsurface (Fig. 7). ²³⁴Th/²³⁸U ratios ranging from 1 to maximum 1.3 clearly indicated fast and intense remineralization of sinking material in the mesopelagic zone (100–600 m), which was further confirmed by parallel biogenic particulate barium data (Fig. 7). Therefore one of the most likely sources of labile Fe(II) in the subsurface might be remineralization/disaggregation of biogenic particles settling from above. Moreover, the very large sub-surface maxima in the STZ were consistent with a bloom in a senescent stage (Ras and Claustre, pers. com.). The value of %Fe(II)/DFe at these depths can be as high as 50–70%, suggesting that biogenic Fe is mainly regenerated as Fe(II) species, as

- already observed in other studies (Hutchins and Bruland, 1994; Sarthou et al., 2008).
 The remineralization of organic matter (OM) is associated with the consumption of oxygen and the apparent oxygen utilization (AOU) can also provide a quantitative estimate of the amount of material that has been remineralized (Sarma et al., 2007). In our study, no coincidence between the sub-surface maxima of labile Fe(II) and AOU was observed (not shown). Indeed, the maxima of AOU were around 1000–1200 m in the STZ and in the ACC north of the PF, and around 300–800 m south of the PF. The very
- ²⁰ STZ and in the ACC north of the PF, and around 300–800 m south of the PF. The very particle reactive ²³⁴Th has a short half-life (24.1 days), and may then help to trace remineralization processes with a much shorter half-life than when using the AOU, and which occur locally.

In the southern part of our transect (stations L6, S4, L7, S5, Fig. 8), the winter waters were strongly visible on the T data and were associated with local minima of labile Fe(II) concentrations. At the end of the winter, the stratification of the water column divides the Antarctic surface waters into two water masses that evolve differently: the Antarctic surface summer waters (AASSW) and the Antarctic winter waters (AAWW). The cold AAWW are less affected by phytoplankton activity and keep the signal of the winter



time. Thus, when the concentrations of a given element in the AAWW is higher than the ones in the AASSW, the variation of concentrations can be assumed to represent the biological uptake (Sarthou et al., 1997; Blain et al., 2007). In our case, labile Fe(II) concentrations are lower in the AAWW. This could reflect processes involving a biological source of Fe(II) in the AASSW and confirm results observed in the SML.

4.2.3 Below 1500 m

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Only two stations showed labile Fe(II) concentrations higher than the detection limit below 1500 m. Station S2 was located at the vicinity of the Agulhas Ridge and local maxima of DFe were observed there (Chever et al., 2010), suggesting hydrothermal or sediment inputs (Elrod et al., 2004; Boyle and Jenkins, 2008; Bennett et al., 2008; 10 Tagliabue et al., 2010). %Fe(II)/DFe was not very high (1.4–5%) and Fe(II) half-life was the lowest of the section (Fig. 3b), suggesting that Fe(II) is continuously provided to the deep waters but reoxidized guite fast. During the ANT XXIV/3 expedition, Klunder et al. (2010) and Middag et al. (2010) evidenced hydrothermal inputs of Fe and Mn in the Bouvet region (52–56°S). The hydrothermal signal was not clearly seen on our DFe 15 (Chever et al., 2010) nor on our labile Fe(II) data, likely due to a lower resolution of our sampling. At station S5, concentrations of labile Fe(II) as high as 0.050 nM were observed at 3500 m, with %Fe(II)/DFe equal to 13%. Along the zero meridian, DFe concentrations in the deep waters north of the Weddell Gyre $(0.47 \pm 0.16 \text{ nM}, n = 98)$, Klunder et al., 2010, and 0.42 ± 0.07 , n = 4, Chever et al., 2010) were higher than south

- ²⁰ Klunder et al., 2010, and 0.42 ± 0.07 , n = 4, Chever et al., 2010) were higher than south of the Weddell Gyre (0.33 ± 0.14 nM, n = 98, Klunder et al., 2010). North of the Weddell Sea Gyre, the deep waters flow eastward, and might have had a recent contact with the northern limit of the Weddell Basin (Orsi et al., 1993; Meredith et al., 2000; Klatt et al., 2005), flowing along the North Weddell Ridge. A local reductive dissolution of
- ²⁵ particles coming from the slope sediments of the ridge may explain the high values of labile Fe(II) at this station.



4.3 Oxidation rates

The Fe(II) half-life values in the surface waters were similar to previous values estimated in natural surface seawater at near-ambient concentrations (6-28 min, Croot et al., 2008). Our values were higher in the deep than in the surface waters. To our knowledge, our study is the first one to measure Fe(II) oxidation rates in natural deep 5 seawater at near-ambient concentrations. The deep values were never as high as the ones estimated by Hansard et al. (2009, up to 690 min) in the Pacific Ocean. However, their $[O_2]$ at ~1000 m were as low as 13 μ M, whereas $[O_2]$ was never lower than 100 μ M along the BGH transect. The overall oxidation rate of Fe(II) is a function of oxidant concentrations (e.g. oxygen, hydrogen peroxide, superoxide, etc., Gonzalez-Davila et al., 2006), T, pH, as well as Fe(II) chemical speciation (mainly Fe^{2+} , $Fe(OH)^+$, $Fe(OH)_2$, $FeCO_3$, $Fe(CO_3)_2^{2-}$, $Fe(CO_3)(OH)^-$, Millero, 1989; King, 1998; Santana-Casiano et al., 2006; Trapp and Millero, 2007). To compare our data with theoretical ones, we used two published models of Fe(II) oxidation kinetics and in situ physical-chemical conditions (Model I: Santana-Casiano et al., 2005; Model II: Trapp and Millero, 2007; see supplementary material for detailed calculations). Theoretical values are given in Table 3. The two models differ in the equations used for the calculations of the oxidation rate constants of the individual species for oxidation by oxygen (see Supplement). Moreover, Model I considers the $Fe(CO_3)(OH)^-$ species, as well as the oxidation by the superoxide. None of the two models considers organic matter effects, and differences 20 in oxidation rates among samples are only related to T, pH, S, and carbonate effects. In the upper waters, for Model I, the Fe(II) half-life times ranged from 7.5 to 18.4 min, with a mean value of 12.4±3.0 min. For Model II, values ranged from 5.5 to 13.6 min,

with a mean value of 12.4 ± 3.0 min. For Model II, values ranged from 5.5 to 13.6 min, with a mean value of 9.5 ± 2.3 min. The ranges of variations of the two theoretical data sets were similar, although a paired-t test showed that the two data sets were significantly different (P < 0.01, n = 12), with values from Model I always higher than values from Model II (up to 5 min). The measured $t_{1/2}$ (2.9–11.3 min, mean value 6.7 ± 2.6 min) showed systematically lower values than the theoretical ones of both models (by up to 10-15 min at station L2), except at station S5 where the measured value was slightly



higher than the Model II one. A much larger difference was observed in the deep waters between the two models. The Model I values ranged from 86 to 138 min (mean value 112 ± 19 min), whereas the Model II ones were about 4 times lower, ranging from 19 to 32 min (mean value 26 ± 5 min). This difference may come from the uncertain-

- ties in the model parameterization and/or on superoxide concentrations which could vary at depth more than oxygen concentration (see Supplement). However, what both models indicated was that in the deep waters, the half life times were almost constant (less than a factor of two) compared to the measured values which varied by a factor of 7 (10–72 min). Indeed, in the deep waters, the pH and *T* ranges of variation are
- relatively small, inducing a small range of variation of theoretical values. The largest range of variation of the measured values could be induced by a change in oxygen concentrations. Indeed, oxygen may have been consumed by micro-organisms in the sample during the 24 h storage or increase if an oxygen contamination occurred. Also, when the oxidation rates were measured at 4 °C, the deep samples and some of the first of the sample samples and some of the first of the sample samples and some of the sample samples.
- ¹⁵ surface samples were heated while most of the surface samples were cooled. These differences can affect the intermediate species and equilibrium processes. Moreover, after heating, changes in pH due to CO₂ dissolution-exchange can modify the Fe(II) speciation.

Another explanation for the variability of the measured t_{1/2} and the discrepancy between measured and theoretical is organic complexation. Although dissolved Fe(III) is now well known to be strongly bound by organic chelators in seawater (Gledhill and van den Berg, 1994; Rue and Bruland, 1997; Gerringa et al., 2006, 2008; Thuróczy et al., 2010), organic complexation of Fe(II) has been suggested but never directly measured (Croot et al., 2007, 2008; Roy et al., 2008). In the Subarctic Pacific, Roy et al. (2008)
observed a significant difference between the measured Fe(II) oxidation rates in natural surface water and the ones in UV-treated surface water, which strongly suggested that organic ligands influenced Fe(II) speciation in seawater. Like for Fe(III) species, the Fe(II) organic speciation may help maintaining Fe(II) in the dissolved phase. However, numerous studies on the effect of Fe organic complexation on the oxidation kinetics



showed that the organic complexation can either increase or decrease the Fe(II) oxidation rates (Rijkenberg et al., 2006 and references herein). Variability of organic compounds within the water column could thus induce variability in the observed oxidation rates.

5 5 Conclusions

Concentrations of labile Fe(II) in the surface waters were systematically higher than the detection limit of our analytical method. The highest values were observed where sampling was done between 12:00 and 16:00, suggesting a biological production of Fe(II) in the SML linked to photosynthesis. South of the section, local minima coinciding with the Winter Waters confirm that direct biological reduction of Fe(III) may occur in the SML. This would explain why our nighttime surface samples have concentrations higher than the detection limit. At intermediate depths, sub-surface maxima were observed all along the section, although more pronounced in the STZ. A bloom at a senescent stage in the STZ, together with a good consistency between the maxima of labile Fe(II) and

- the increase in ²³⁴Th/²³⁸U towards values over 1 suggested that Fe remineralization occurred at those depths and that Fe was mainly regenerated as Fe(II) species. In the deep waters, labile Fe(II) concentrations were higher than the detection limit at two stations: one located at the vicinity of the Agulhas ridge and another one in the north of the Weddell Gyre. Here we propose that this was likely due to hydrothermal
- and/or sediment inputs. Fe(II) oxidation rates were measured in the surface and deep waters. Our study is the first one, to our knowledge, to measure Fe(II) oxidation rates in natural deep seawater at near-ambient concentrations. In the deep waters, $t_{1/2}$ values were on average 6 times higher than in the surface waters. The comparison of our measured $t_{1/2}$ with theoretical ones using two different models suggested that
- organic complexation may strongly influence the oxidation rates, although more studies are needed to better constrain the organic speciation of Fe(II) and its influence on the half-lifes of Fe(II). The global data set of Fe(II) also needs to be increased and this will be done in the framework of the GEOTRACES programme and the associated cruises.





Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/8/4163/2011/ bgd-8-4163-2011-supplement.pdf.

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References

¹⁵ Alldredge, A. L. and Cohen, Y.: Can microscale patches persist in the sea?, Microelectrode study of marine snow, feacal pellets, Science, 235, 689–601, 1987.

Arhan, M., Mercier, H., and Park, Y.: On the deep water circulation of the eastern South Atlantic Ocean, Deep Sea Res. Pt. I, 50(7), 889–916, 2003.

Arhan, M., Speich, S., Dencausse, G., Messager, C., Fine, R., and Boye, M.: Anticyclonic and

- 20 cyclonic eddies of subtropical origin in the subantarctic zone south of Africa, submitted to J. Geophys. Res. Oceans, 2011.
 - Barbeau, K., Rue, E. L., Bruland, K. W., and Butler, A.: Photochemical cycling of iron in the surface ocean mediated by microbial iron(III)-binding ligands, Nature, 413, 409–413, 2001.

Bennett, S. A., Achterberg, E. P., Connelly, D. P., Statham, P. J., Fones, G. R., and German,

C. R.: The distribution and stabilisation of dissolved Fe in deep-sea hydrothermal plumes, Earth Planet. Sci. Lett., 270(3–4), 157–167, 2008.

Blain, S., Quéguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., Bowie, A., Brunet, C., Brussaard, C., Carlotti, F., Christaki, U., Corbière, A., Durand, I., Ebersbach, F., Fuda,



J.-L., Garcia, N., Gerringa, L., Griffiths, B., Guigue, C., Guillerm, C., Jacquet, S., Jeandel, C., Laan, P., Lefèvre, D., Lomonaco, C., Malits, A., Mosseri, J., Obernosterer, I., Park, Y.-H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., Savoye, N., Scouarnec, L., Souhaut, M., Thuiller, D., Timmermans, K., Trull, T., Uitz, J., van-Beek, P., Veldhuis, M., Vincent, D., Viollier, E., Vong, L., and Wagener, T.: Impact of natural iron fertilisation on carbon sequestration in the Southern Ocean, Nature, 7139, 1070–1074, 2007. Boebel, O., Lutjeharms, J., Schmid, C., Zenk, W., Rossby, T., and Barron, C.: The Cape Caul-

5

dron: a regime of turbulent inter-ocean exchange, Deep-Sea Res. Pt. II, 50, 57-86, 2003. Bowie, A. R., Achterberg, E. P., Sedwick, P. N., Ussher, S., and Worsfold, P. J.: Real-time

- monitoring of picomolar concentrations of iron(II) in marine waters using automated flow 10 injection chemiluninescence instrumentation. Environ. Sci. Technol., 36, 4600–4607, 2002. Boyd, P.: Ironing out algal issues in the southern ocean, Science, 304(5669), 396-397, 2004. Boyd, P. W. and Ellwood, M. J.: The biogeochemical cycle of iron in the ocean, Nat. Geosci., 3. 675-682. doi:10.1038/NGEO964. 2010.
- Bovd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R., Bakker, D. C. 15 E., Bowie, A., Buesseler, K. O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R. M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., and Zeldis, J.: A mesoscale
- phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, Nature, 20 407, 695–702, 2000.
 - Boye, M., Aldrich, A., van den Berg, C. M. G., de Jong, J. T. M., Veldhuis, M., and de Baar, H. J. W.: Horizontal gradient of the chemical speciation of iron in surface waters of the northeast Atlantic Ocean, Mar. Chem., 80, 129-143, 2003.
- Boye, M., Aldrich, A., van den Berg, C. M. G., de Jong, J. T. M., Nirmaier, H., Veldhuis, M., 25 Timmermans, K. R., and de Baar, H. J. W.: The chemical speciation of iron in the north-east Atlantic Ocean, Deep Sea Res. Pt. I, 53, 667-683, 2006.

Boyle, E. and Jenkins, W., Hydrothermal Iron in the Deep Western South Pacific, Geochim. Cosmochim. Ac., 72(12), Supplement 1, A107, 2008.

Bruland, K. W. and Rue, E. L.: Analytical Methods for the Determination of Concentrations 30 and Speciation of Iron, edited by: Turner, S. and Hunter, K. A., Biogeochemistry of Fe in Seawater, SCOR/IUPAC, 255-290, 2001,

Bucciarelli, E., Sarthou, G., and Chever, F.: Hydrogen peroxide distributions along a transect



Discussion

from the subtropical domain to the Weddell Sea Gyre in the Atlantic sector of the Southern Ocean, in prep., 2011.

- Cai, P. H., Chen, W. F., Dai, M. H., Wan, Z. W., Wang, D. X., Li, Q., Tang, T. T., and Lv, D. W.: A high resolution study of particle export in the southern South China Sea based on ²³⁴Th²³⁸U
- ⁵ disequilibrium, J. Geophys. Res. Ocean., 113(C4), C04019, doi:10.1029/2007JC004268, 2008.
 - Chever, F., Bucciarelli, E., Sarthou, G., Speich, S., Arhan, M., Penven, P., and Tagliabue, A.: Physical speciation of iron in the Atlantic sector of the Southern Ocean, along a transect from the subtropical domain to the Weddell Sea Gyre, J. Geophys. Res. Ocean, 115, C10059, doi:10.1029/2009JC005880, 2010.
 - Chin, C. S., Coale, K. H., Elrod, V. A., and Johnson, K. S.: In situ observations of dissolved iron and manganese in hydrothermal vent plumes, Juan de Fuca Ridge, J. Geophys. Res., 99(B3), 4969–4984, 1994.

10

15

Coale, K. H., Chin, C. S., Massoth, G. J., Johnson, K. S., and Baker, E. T.: In-situ chemical mapping of dissolved iron and manganese in hydrothermal plumes, Nature, 352, 325–328,

- 1991. Coale, K. H., Johnson, K. S., Fitzwater, S. E., Gordon, R. M., Tanner, S., Chavez, F. P., Ferioli, L., Sakamoto, C., Rogers, P., Millero, F., Steinberg, P., Nightingale, P., Cooper, D., Cochlan, W. P., Landry, M. R., Constantinou, J., Rollwagen, G., Trasvina, A., and Kudela, R.: A mas-
- sive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, Nature, 383, 495–501, 1996.
 - Coale, K. H., Johnson, K. S., Chavez, F. P., Buesseler, K. O., Barber, R. T., Brzezinski, M. A., Cochlan, W. P., Millero, F. J., Falkowski, P. G., Bauer, J. E., Wanninkhof, R. H., Kudela, R. M., Altabet, M. A., Hales, B. E., Takahashi, T., Landry, M. R., Bidigare, R. R., Wang, X. J.,
- ²⁵ Chase, Z., Strutton, P. G., Friederich, G. E., Gorbunov, M. Y., Lance, V. P., Hilting, A. K., Hiscock, M. R., Demarest, M., Hiscock, W. T., Sullivan, K. F., Tanner, S. J., Gordon, R. M., Hunter, C. N., Elrod, V. A., Fitzwater, S. E., Jones, J. L., Tozzi, S., Koblizek, M., Roberts, A. E., Herndon, J., Brewster, J., Ladizinsky, N., Smith, G., Cooper, D., Timothy, D., Brown, S. L., Selph, K. E., Sheridan, C. C., Twining, B. S., and Johnson, Z. I.: Southern ocean iron enrichment experiment: Carbon cycling in high- and low-Si waters, Science, 304(5669), 408–414, 2004.
 - Croot, P. L. and Laan, P.: Continuous shipboard determination of Fe(II) in polar waters using flow injection analysis with chemiluminescence detection, Anal. Chim. Acta, 466(2), 261–



273, 2002.

15

- Croot, P. L., Bowie, A. R., Frew, R. D., Maldonado, M. T., Hall, J. A., Safi, K. A., La Roche, J., Boyd, P. W., and Law, C. S.: Retention of dissolved iron and Fe-II in an iron induced Southern Ocean phytoplankton bloom, Geophys. Res. Lett., 28(18), 3425–3428, 2001.
- ⁵ Croot, P. L., Laan, P., Nishioka, J., Strass, V., Cisewski, B., Boye, M., Timmermans, K. R., Bellerby, R. G., Goldson, L., Nightingale, P., and de Baar, H. J. W.: Spatial and temporal distribution of Fe(II) and H₂O₂ during EisenEx, an open ocean mescoscale iron enrichment, Mar. Chem., 95, 65–88, 2005.

Croot, P. L., Frew, R. D., Sander, S., Hunter, K. A., Ellwood, M. J., Pickmere, S. E., Abraham, E.

- R., Law, C. S., Smith, M. J., and Boyd, P. W.: Physical mixing effects on iron biogeochemical cycling: Fe-Cycle experiment, J. Geophys. Res., 112(C06015), doi:10.1029/2006JC003748, 2007.
 - Croot, P. L., Bluhm, K., Schlosser, C., Streu, P., Breitbarth, E., Frew, R., and Ardelan, M. V.: Regeneration of Fe(II) during EIFeX and SOFeX, Geophys. Res. Lett., 35, L19606, doi:10.1029/2008GL035063, 2008.
- de Baar, H. J. W. and de Jong, J. T. M.: Distributions, Sources and Sinks of Iron in Seawater, in: Biogeochemistry of Fe in Seawater, edited: Turner, D. R. and Hunter, K. A., SCOR-UPAC series, J. Wiley, Baltimore, 123–253, 2001.

Ducet, N., Traon, P. Y. L., and Reverdin, G.: Global high-resolution mapping of ocean circulation

from TOPEX/Poseidon and ERS-1 and -2, J. Geophys. Res., 105(C8), 19477–19498, 2000. Elrod, V. A., Berelson, W. M., Coale, K. H., and Johnson, K. S.: The flux of iron from continental shelf sediments: A missing source for global budgets, Geophys. Res. Lett., 31, L12307, doi:10.1029/2004GL020216, 2004.

Field, M. P. and Sherrell, R. M.: Dissolved and particulate Fe in a hydrothermal plume at 9°45' N,

- East Pacific Rise: Slow Fe (II) oxidation kinetics in Pacific plumes, Geochim. Cosmochim. Ac., 64(4), 619–628, 2000.
 - Gerringa, L. J. A., Veldhuis, M. J. W., Timmermans, K. R., Sarthou, G., and de Baar, H. J. W.: Co-variance of dissolved Fe-binding ligands with biological observations in the Canary Basin., Mar. Chem., 102, 276–290, 2006.
- ³⁰ Gerringa, L. J. A., Blain, S., Laan, P., Sarthou, G., Veldhuis, M. J. W., Viollier, E., and Timmermans, K. R.; Dissolved organic ligands of Fe near the Kerguelen Archipelago in the Southern Ocean (Indian sector), Deep Sea Res. Pt. II, 55(5–7), 606–621, 2008.

Gervais, F., Riebesell, U., and Gorbunov, M. Y.: Changes in primary productivity and chlorophyll



a in response to iron fertilization in the Southern Polar Frontal Zone, Limnol. Oceanogr., 47(5), 1324–1335, 2002.

- Gladyshev, S., Arhan, M., Sokov, A., and Speich, S.: A hydrographic section from South Africa to the southern limit of the Antarctic Circumpolar Current at the Greenwich meridian, Deep
- ⁵ Sea Res. Pt. I, 55, 1284–1303, 2008.

10

Gledhill, M. and van den Berg, C. M. G.: Determination of complexation of iron(III) with natural organic complexing ligands in seawater using cathodic stripping voltammetry, Mar. Chem., 47, 41–54, 1994.

Gledhill, M. and van den Berg, C. M. G.: Measurement of the redox speciation of iron in seawater by catalytic cathodic stripping voltammetry, Mar. Chem., 50(1–4), 51–62, 1995.

- Gobler, C. J., Donat, J. R., Consolvo, J. A., and Sanudo, W. S. A.: Physicochemical speciation of iron during coastal algal blooms, Mar. Chem., 77(1), 71–89, 2002.
- Godrant, A., Rose, A. L., Sarthou, G., and Waite, T. D.: A new method for the determination of extracellular production of superoxide from phytoplankton cells using the chemiluminescence probes MCLA and the Red-CLA. Limnol. Oceanogr.-Meth., 7, 682–692, 2009.
- probes MCLA and the Red-CLA, Limnol. Oceanogr.-Meth., 7, 682–692, 2009.
 Gonzalez-Dávila, M., Santana-Casiano, J. M., and Millero, F. J.: Oxidation of iron (II) nanomolar with H₂O₂ in seawater, Geochim. Cosmochim. Ac., 69, 83–93, 2005.
 - Gonzalez-Dávila, M., Santana-Casiano, J. M., and Millero, F. J.: Competition between O_2 and H_2O_2 in the oxidation of Fe(II) in natural waters, J. Sol. Chem., 35, 95–111, 2006.
- Gonzalez-Dávila, M., Santana-Casiano, J. M., Rueda, M. J., Llinás, O., and Gonzalez-Dávila, E. F.: Seasonal and interannual variability of seasurface carbon dioxide species at the European Station for Time Series in the Ocean at the Canary Islands (ESTOC) between 1996 and 2000, Global Biogeochem. Cy., 17(3), 1076, doi:10.1029/2002GB001993, 2003.

Gordon, A. L., Weiss, R. F., Smethie, J. W. M., and Warner, M. J.: Thermocline and intermediate water communication between the South Atlanctic and Indian Oceans, J. Geophys. Res., 97(C5), 7223–7240, 1992.

- Hansard, S. P., Landing, W. M., Measures, C. I., and Voelker, B. M.: Dissolved iron(II) in the Pacific Ocean: Measurements from the PO2 and P16NCLIVAR/CO2 repeat hydrography expeditions, Deep Sea Res. Pt. I, 56, 1117–1129, 2009.
- Hansard, S. P., Vermilyea, A. W., and Voelker, B. M.: Measurements of superoxide radical concentration and decay kinetics in the Gulf of Alaska, Deep-Sea Res. Pt. I, 57, 1111–1119, 2010.

Hong, H. and Kester, D. R.: Redox state of iron in the offshore waters of Peru, Limnol.



Oceanogr., 31, 512-524, 1986.

5

10

20

Hopkison, B. M. and Barbeau, K. A.: Organic and Redox speciation of iron in the tropical North Pacific suboxic zone, Mar. Chem., 106, 2–17, 2007.

Hutchins, D. A. and Bruland, K. W.: Grazer-mediated regeneration and assimilation of Fe, Zn, and Mn from planktonic prey, Mar. Ecol. Prog. Ser., 110, 259–269, 1994.

Hutchins, D. A., DiTullio, G. R., and Bruland, K. W.: Iron and regenerated production: Evidence for biological iron recycling in two marine environments, Limnol. Oceanogr., 38(6), 1242–1255, 1993.

Hutchins, D. A., Wang, W., and Fisher, N. S.: Copepod grazing and the biogeochemical fate of diatom iron, Limnol. Oceanogr., 40, 989–994, 1995.

Johnson, K. S., Coale, K.H., Elrod, V.A., and Tindale, N.W.: Iron Photochemistry in seawater from the Equatorial Pacific, Mar. Chem., 46, 319–334, 1994.

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

- Journet, E., Desboeufs, K. V., Sofikitis, A., Varrault, G., and Colin, J.-L.: In situ speciation of trace Fe(II) and Fe(III) in atmospheric waters by the FZ method coupled to GFAAS analysis, Int. J. Environ. Anal. Chem., 87(9), 647–658, 2007.
 - Kieber, R.J., Williams, K., Willey, J. D., Skrabal, S., Avery, G., and R. B. J.: Iron speciation in coastal rainwater: concentration and deposition to seawater, Mar. Chem., 73(2), 83–95, 2001.
 - King, D. W.: Role of carbonate speciation on the oxidation rate of Fe(II) in aquatic systems, Environ. Sci. Technol., 32, 2997–3003, 1998.
 - King, D. W., Aldrich, R. A., and Charnecki, S. E.: Photochemical redox cycle of iron in NaCl solutions, Mar. Chem., 44, 105–120, 1993.
- ²⁵ King, D. W., Lounsbury, H. A., and Millero, F. J.: Rate and mechanism of Fe(II) oxidation at nanomolar total iron concentration, Environ. Sci. Technol., 29(3), 818–824, 1995.
 - Klatt, O., Fahrbach, E., Hoppema, M., and Rohardt, G.: The transport of the Weddell Gyre across the Prime meridian, Deep Sea Res. Pt. II, 52, 513–528, doi:10.1016/j.dsr2.2004.12.015, 2005.
- Klunder, M., Laan, P., Middag, R., Baar, H. J. W. D., and Ooijen, J. V.: Dissolved Iron the Southern Ocean (Atlantic Sector), Deep Sea Res. Pt. II, in press, doi:10.1016/j.dsr2.2010.10.042, 2010.

Kuma, K., Nakabayashi, S., Suzuki, Y., Kudo, I., and Matsunaga, K.: Photoreduction of Fe(III)



4189

by dissolved organic substances and existence of Fe(II) in seawater during spring blooms, Mar. Chem., 37, 15–27, 1992a.

- Kuma, K., Nakabayashi, S., Suzuki, Y., and Matsunaga, K.: Dissolution rate and solubility of colloidal hydrous ferric oxide in seawater, Mar. Chem., 38, 133–143, 1992b.
- ⁵ Kuma, K., Nishioka, J., and Matsunaga, K.: Controls on iron(III) hydroxide solubility in seawater: the influence of pH and natural organic ligands, Limnol. Oceanogr., 41(3), 396–407, 1996.
 - Kustka, A. B., Shaked, Y., Milligan, A. J., King, D. W., and Morel, F. M. M.: Extracellular production of superoxide by marine diatoms: Contrasting effects on iron redox chemistry and bioavailability, Limnol. Oceanogr., 50(4), 1172–1180, 2005.
- Legendre, L., Demers, S., Garside, C., Haugen, E. M., Phinney, D. A., Shapiro, L. P., Therriault, J. C., and Yentsch, C. M.: Circadian photosynthetic activity of natural marine phytoplankton isolated in a tank, J. Plankton Res., 10, 1–6, 1988.
 - Lewis, E. and Wallace, D. W. R.: Program Developed for CO₂ System Calculations. ORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 1998.
- oratory, US Department of Energy, Oak Ridge, Tennessee, 1998.
 Liu, X. and Millero, F. J.: The solubility of iron in seawater, Mar. Chem., 77(1), 43–54, 2002.
 Lohan, M. C. and Bruland, K. W.: Elevated Fe(II) and dissolved Fe in hypoxic shelf waters off Oregon and Washington: An enhanced source of iron to coastal upwelling regimes, Environ. Sci. Technol., 42(17), 6462–6468, 2008.
- Maiti, K., Benitez-Nelson, C. R., and Buesseler, K. O.: Insights into particle formation and remineralization using the short-lived radionuclide, Thoruim-234, Geophys. Res. Lett., 37, L15608, doi:10.1029/2010GL044063, 2010.
 - Maldonado, M. T. and Price, N. M.: Reduction and transport of organically bound iron by *Thalassiosira oceanica* (Bacillariophyceae), J. Phycol., 37(2), 298–309, 2001.
- Maldonado, M. Y. and Price, N. M.: Utilization of iron bound to strong organic ligands by plankton communities in the subarctic Pacific Ocean, Deep Sea Res. Pt. II, 46(11–12), 2447–2473, 1999.

30

- Maldonado, M. T., Allen, A. E., Chong, J. S., Lin, K., Leus, D., Karpenko, N., and Harris, S. L.: Copper-dependent iron transport in coastal and oceanic diatoms, Limnol. Oceanogr., 51(4), 1729–1743. 2006.
- Meredith, M. P., Locarnini, R. A., Scoy, K. A. V., Watson, A. J., Heywood, K. J., and King, B. A.: On the sources of Weddell Gyre Antarctic Bottom Water, J. Geophys. Res., 105(C1), 1093–1104, 2000.



Middag, R., Baar, H. J. W. d., Laan, P., Cai, P. H., and van Ooijen, J. C.: Dissolved manganese in the atlantic sector of the Southern Ocean, Deep Sea Res. Pt. II, in press, doi:10.1016/j.dsr2.2010.10.043, 2010.

Millero, F. J.: Effect of ionic interactions on the oxidation of iron(II) and copper(I) in natural waters, Mar. Chem., 28, 1–18, 1989.

Millero, F. J. and Sotolongo, S.: The oxidation of Fe(II) with H₂O₂ in seawater, Geochim. Cosmochim. Ac., 53, 1867–1873, 1989.

5

20

- Millero, F. J., Sotolongo, S., and Izaguirre, M.: The oxidation kinetics of Fe(II) in seawater, Geochim. Cosmochim. Ac., 51, 793–801, 1987.
- Mintrop, L., Pérez, F. F., González Dávila, M., Körtzinger, A., and Santana- Casiano, J. M.: Alkalinity determination by potentiometry: intercalibration using three different methods, Cien. Mar., 26, 23–37, 2000.
 - Moffett, J., Goepfert, T. J., and Naqvi, W. A.: Reduced iron associated with secondary nitrite maxima in the Arabian Sea, Deep Sea Res. Pt. I, 54, 1341–1349, 2007.
- ¹⁵ Morel, F. M. M., Kustka, A. B., and Shaked, Y.: The role of unchelated Fe in the iron nutrition of phytoplankton, Limnol. Oceanogr., 53(1), 400–404, 2008.
 - O'Sullivan, D. W., Hanson, A. K., Miller, W. L., and Kester, D. R.: Measurement of Fe(II) in equatorial Pacific surface seawater, Limnol. Oceanogr., 36(8), 1727–1741, 1991.

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

- Orsi, A. H., Nowlin, W. D., and Whitworth III, T.: On the circulation and stratification of the Weddell Gyre, Deep Sea Res. Pt. I, 40, 169–203, 1993.
- Ozsoy, T. and Saydam, A. C.: Iron speciation in precipitation in the north-eastern Mediterranean and its relationship with Sahara dust, J. Atmos. Chem., 40, 41–76, 2001.
- Planchon F., Cavagna A. J., Cardinal, D., and Dehairs, F.: Dynamics of biogenic particles in the Southern Atlantic Ocean as revealed by ²³⁴Th proxy along the Bonus-Good-Hope transect from Cape Basin to Northern Weddell gyre, submitted to Biogeosciences, 2011.
 - Pollard, R., Sanders, R., Lucasa, M., and Statham, P.: The Crozet Natural Iron Bloom and Export Experiment (CROZEX), Deep Sea Res. Pt. II, 54(18–20), 1905–1914, 2007.
- ³⁰ Rich, H. W. and Morel, F. M. M.: Availability of well-defined iron colloids to the marine diatom Thalassiosira weissflogii, Limnol. Oceanogr., 35(3), 652–662, 1990.
 - Rijkenberg, M. J. A., Gerringa, L. J. A., Carolus, V. E., Velzeboer, I., and de Baar, H. J. W.: Enhancement and inhibition of iron photoreduction by individual ligands in open ocean sea-



Discussion Paper

Discussion Paper

Discussion Paper

Discussion

Paper

water, Geochim. Cosmochim. Ac., 70, 2790-2805, 2006.

- Rose, A. L. and Waite, T. D.: Chemiluminescence of luminol in the persence of iron(II) and oxygen: Oxidation mechanism and implications for its analytical use, Anal. Chem., 73, 5909–5920, 2001.
- ⁵ Rose, A. L. and Waite, T. D.: Kinetic model for Fe(II) oxidation in seawater in the absence and presence of natural organic matter, Environ. Sci. Technol., 36, 433–444, 2002.

Rose, A. L. and Waite, T. D.: Predicting iron speciation in coastal waters from the kinetics of sunlight-mediated iron redox cycling, Aquat. Sci., 65, 375–383, 2003.

Rose, A. L., Salmon, T. P., Lukondeh, T., Neilan, B. A., and Waite, T. D.: Use of Superoxide as

- an Electron Shuttle for Iron Acquisition by the Marine Cyanobacterium *Lyngbya majuscula*, Environ. Sci. Technol., 39(10), 3708–3715, doi:10.1021/es048766c, 2005.
 - Roy, E. G., Wells, M. L., and King, D. W.: Persistence of iron(II) in surface waters of the western subarctic Pacific, Limnol. Oceanogr., 53, 89–98, 2008.

Rue, E. L. and Bruland, K. W.: The role of organic complexation on ambient iron chemistry

- ¹⁵ in the equatorial Pacific Ocean and the response of a mesoscale iron addition experiment, Limnol. Oceanogr., 42(5), 901–910, 1997.
 - Rutgers van der Loeff., M. M., Cai, P. H., Stimac, I., Bracher, A., Middag, R., Klunder, M. B., and Van Heuven, S.: ²³⁴Th in surface waters: distribution of particle export flux across the Antarctic Circumpolar Current and in the Weddell Sea during the GEOTRACES expedition
- ZERO and DRAKE, Deep-Sea Res. Pt. II, in press, doi:10.1016/j.dsr2.2011.02.004, 2011. Salmon, T. P., Rose, A. L., Neilan, B. A., and Waite, T. D.: The FeL model of iron acquisition: Nondissociative reduction of ferric complexes in the marine environment, Limnol. Oceanogr., 51(4), 1744–1754, 2006.

Santana-Casiano, J. M., Gonzalez-Davila, M., and Millero, F. J.: The oxidation of Fe(II) in NaCl-

- HCO₃- and seawater solutions in the presence of phthalate and salicylate ions: a kinetic model, Mar. Chem., 85 (1–2), 27–40, 2004.
 - Santana-Casiano, J. M., Gonzalez-Davila, M., and Millero, F. J.: Oxidation of nanomolar levels of Fe(II) with oxygen in natural waters, Environ. Sci. Technol., 39, 2073–2079, 2005.

Santana-Casiano, J. M., Gonzalez-Davila, M., and Millero, F. J.: The role of Fe(II) species on

- the oxidation of Fe(II) in natural waters in the presence of O_2 and H_2O_2 , Mar. Chem., 99, 70–82, 2006.
 - Sarma, V. V. S. S., Kumar, M. D., and Saino, T.: Impact of sinking carbon flux on accumulation of deep-ocean carbon in the Northern Indian Ocean, Biogeochem., 82, 89–100,



doi:10.1007/s10533-006-9055-1, 2007.

15

20

- Sarthou, G., Jeandel, C., Brisset, L., Amouroux, D., and Donard, O. F. X.: Fe and H₂O₂ distributions in the upper 250 meters of the water column in the Indian sector of the Southern Ocean, Earth Planet. Sci. Lett., 147, 83-92, 1997.
- 5 Sarthou, G., Baker, A. R., Blain, S., Achterberg, E. P., Boye, M., Bowie, A. R., Croot, P. L., Laan, P., de Baar, H. J W., Jickells, T. D., and Worsfold, P. J.: Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean, Deep Sea Res. Pt. I, 50(10–11), 1339–1352, 2003.

Sarthou, G., Vincent, D., Christaki, U., Obernosterer, I., Timmermans, K. R., and Brussaard, C.

P. D.: The fate of biogenic iron during a phytoplankton bloom induced by natural fertilization: 10 impact of copepod grazing, Deep Sea Res. Pt. II, 55, 734-751, 2008.

Shaked, Y., Kustka, A. B., Morel, F. M. M., and Erel, Y.: Simultaneous determination of iron reduction and uptake by phytoplankton, Limnol. Oceanogr.-Meth., 2, 137-145, 2004.

Speich, S., Arhan, M., Gladyshev, S., Rupolo, V. and Perrot, X.: Upper layer structure and dynamics along BGH, submitted to Ocean Sci., 2011,

Statham, P. J., German, C. R.m and Connelly, D.P.: Iron(II) distribution and oxidation kinetics in hydrothermal plumes at the Kairei and Edmond vent sites, Indian Ocean, Earth Planet. Sci. Lett., 236, 588-596, 2005.

Sunda, W. G.: Trace metal interactions with marine phytoplankton, Biol. Oceanogr., 6, 411–442, 1989.

- Tagliabue, A., Bowie, A., Chever, F., Baptiste, P.-J., Dutay, J.-C., Bucciarelli, E., Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., and Bopp, L.: On the importance of hydrothermalism to the oceanic dissolved iron inventory, Nat. Geosci., 3, 252-256, doi:10.1038/NGEO818, 2010.
- Thuróczy, C.-E., Gerringa, L. J. A., Klunder, M. B., Middag, R., Laan, P., Timmermans, K. R., 25 and de Baar, H. J. W.: Speciation of Fe in the Eastern North Atlantic Ocean, Deep Sea Res. Pt. I, 57(11), 1444–1453, 2010.

Trapp, J. M. and Millero, F. J.: The oxidation of iron(II) with oxygen in NaCl brines, J. Sol. Chem., 36. 1479–1493. 2007.

Tsuda, A., Takeda, S., Saito, H., Nishioka, J., Nojiri, Y., Kudo, I., Kiyosawa, H., Shiomoto, A., 30 Imai, K., Ono, T., Shimamoto, A., Tsumune, D., Yoshimura, T., Aono, T., Hinuma, A., Kinugasa, M., Suzuki, K., Sohrin, Y., Noiri, Y., Tani, H., Deguchi, Y., Tsurushima, N., Ogawa, H., Fukami, K., Kuma, K., and Saino, T.: A mesoscale iron enrichment in the western Subarctic



Discussion Paper

Discussion Paper

Discussion Paper

Pacific induces a large centric diatom bloom, Science, 300, 958-961, 2003.

- Ussher, S. J., Yaqoob, M., Achterberg, E. P., Nabi, A., and Worsfold, P. J.: Effect of model ligands on iron redox speciation in natural waters using flow injection with luminol chemiluminescence detection, Anal. Chem., 77(7), 1971–1978, 2005.
- ⁵ Ussher, S. J., Worsfold, P. J., Achterberg, E. P., Laes, A., Blain, S., Laan, P., and de Baar, H. J. W.: Distribution and redox speciation of dissolved iron on the European continental margin, Limnol. Oceanogr., 52(6), 2530–2539, 2007.
 - Voelker, B. M. and Sedlak, D. L.: Iron reduction by photoproduced superoxide in seawater, Mar. Chem., 50(1–4), 93–102, 1995.
- ¹⁰ Waite, T. D. and Morel, F. M. M.: Coulorimetric study of the redox dynamics of iron in seawater, Anal. Chem., 56, 787–792, 1984.
 - Waite, T. D., Szymczak, R., Espey, Q. I., and Furnas, M. J.: Diel variations in iron speciation in northern Australian shelf waters, Mar. Chem., 50(1–4), 79–92, 1995.
 - Wells, M. L., Mayer, L. M., Donard, O. F. X., de Souza Sierra, M. M., and Ackelson, S. G.: The photolysis of colloidal iron in the oceans, Nature, 353, 248–250, 1991.
- Whitworth III, T. and Nowlin, J. W. D.: Water masses and currents of the Southern Ocean at the Greenwich Meridian, J. Geophys. Res., 96(C6), 6462–6476, 1987.

15

20

- Windom, H. L., Moore, W. S., Niencheski, L. F. H., and Jahnke, R. A.: Submarine groundwater discharge: a large, previously unrecognized source of dissolved iron to the South Atlantic Ocean, Mar. Chem., 102, 252–266, 2006.
- Yuan, J. and Shiller, A. M.: Determination of Subnanomolar Levels of Hydrogen Peroxide in Seawater by Reagent-Injection Chemiluminescence Detection, Anal. Chem., 71, 1975– 1980, 1999.

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Table 1. Location of the stations sampled during the cruise in relation to the domains and fronts crossed. Mixed layer depth observed from the vertical profile of temperature for nearby CTD station, as well as day and time of sampling are indicated. Dates are in DD/MM/YYYY format (D = day, M = month and Y = year).

Oceanographic Domain	Fronts crossed	Station	Position	MLD (m)	Day of sampling	Time of sampling
Subtropical		L1	34.43° S, 14.40° E	50–60	17/02/2008	10:50
-		S1	36.50° S, 13.10° E	40–50	20/02/2008	00:15
		L2	41.18° S, 09.92° E	25	25/02/2008	23:15
	S-STF		42.2° S			
ACC		S2	42.47° S, 08.93° E	50–80	27/02/2008	18:30
	SAF		44.2° S			
		L3	44.88° S, 06.88° E	60–80	01/03/2008	17:45
		L4	46.02° S, 05.87° E	80	03/03/2008	05:40
		S3	47.55° S, 04.37° E	80-100	05/03/2008	15:50
		L5	49.03° S, 02.84° E	100–110	07/03/2008	16:30
	PF		50.2° S			
		L6	50.38° S, 01.33° E	60–80	09/03/2008	04:05
	SACCF		51.5° S			
		S4	51.85° S, 00.00° E	120–150	10/03/2008	12:10
		L7	55.23° S, 00.03° E	80–110	13/03/2008	22:30
	Sbdy		55.5° S			
Eastern part of the Weddell Sea Gyre (EWSG)	-	S5	57.55° S, 00.03° W	100	16/03/2008	16:00

BGD 8, 4163-4208, 2011 Labile Fe(II) concentrations in the **South Atlantic** G. Sarthou et al. **Title Page** Abstract Introduction Conclusions References Tables Figures 14 < Close Back Full Screen / Esc **Printer-friendly Version** Interactive Discussion

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Table 2. Labile Fe(II) concentrations and percentage of labile Fe(II) over dissolved Fe (DFe, Chever et al., 2010). Uncertainties on the concentrations correspond to standard deviation of a same sample measured 3 times. EWSG = eastern part of the Weddell Sea Gyre. nd = not determined, when no DFe data were available.

Subtropical L1 34.43° S, 14.40° E 4505 20 0.017 0.001 7.2 0.6 40 0.016 0.001 3.2 0.2 66 0.025 0.001 nd 80 0.063 0.003 30.1 1.8 200 0.076 0.004 10.2 0.5 700 0.033 0.002 7.7 0.5 1000 0.035 0.002 7.7 0.5 1000 0.035 0.002 5.4 0.3 1200 0.017 0.001 2.1 0.1 2.7 0.2 800 0.038 0.002 5.5 0.3 30 0.039 0.002 5.5 0.3 300 0.117 0.005 nd 1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 1.3 0.2 1400 0.015 0.01 2.0 0.1 1000 0.039 0.002 1.3 0.3 1200 <	Domain	Station	Position	Bottom depth (m)	Depth (m)	Fe(II) (nM)	STD (nM)	Fe(II)/DFe (%)	STD (%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Subtropical	L1	34.43° S, 14.40° E	4505	20	0.017	0.001	7.2	0.6
60 0.025 0.001 nd 80 0.063 0.003 30.1 1.8 200 0.076 0.004 10.2 0.5 700 0.033 0.002 2.8 0.2 800 0.049 0.002 7.7 0.5 1000 0.035 0.002 5.4 0.3 1200 0.017 0.001 2.7 0.2 2100 0.014 0.001 2.1 0.1 1200 0.017 0.001 2.7 0.2 2100 0.014 0.001 2.1 0.1 1200 0.038 0.002 5.5 0.3 300 0.039 0.002 5.5 0.4 40 0.099 0.005 nd 1000 0.038 0.002 3.0 300 0.112 0.006 nd 1020 0.028 0.01 3.1 0.2 1000 0.039 0.000 1.3 0.3 </td <td></td> <td></td> <td></td> <td></td> <td>40</td> <td>0.016</td> <td>0.001</td> <td>3.2</td> <td>0.2</td>					40	0.016	0.001	3.2	0.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					60	0.025	0.001	nd	
L2 41.18°S 09.92°E 4525 L2 41.18°S 09.92°E					80	0.063	0.003	30.1	1.8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					200	0.076	0.004	10.2	0.5
800 0.049 0.002 7.7 0.5 1000 0.035 0.002 5.4 0.3 1200 0.017 0.001 2.7 0.2 2100 0.014 0.001 2.1 0.1 S1 36.50°S 13.10°E 4915 20 0.038 0.002 5.5 0.3 30 0.039 0.002 5.5 0.4 40 0.099 0.005 nd 700 0.107 0.005 nd 300 0.112 0.006 nd 300 0.107 0.005 nd 1000 0.039 0.002 3.9 0.3 31200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3050 0.009 0.000 1.6 0.1 3050					700	0.033	0.002	2.8	0.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					800	0.049	0.002	7.7	0.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					1000	0.035	0.002	5.4	0.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					1200	0.017	0.001	2.7	0.2
S1 36.50° S 13.10° E 4915 20 0.038 0.002 5.5 0.3 30 0.099 0.005 nd 40 0.099 0.005 nd 70 0.107 0.005 nd 300 0.017 0.005 nd 700 0.017 0.005 nd 300 0.017 0.005 nd 1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3050 0.009 0.000 1.6 0.1 3050 0.009 0.000 1.6 0.1 3050 0.099 0.0					2100	0.014	0.001	2.1	0.1
30 0.039 0.002 5.5 0.4 40 0.099 0.005 nd 70 0.107 0.005 nd 300 0.112 0.006 nd 300 0.112 0.005 nd 500 0.107 0.005 nd 700 0.091 0.005 nd 1000 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3050 0.009 0.000 1.6 0.1 3050 0.009 0.000 1.6 0.1 3000 0.009 0.000 1.6 0.1 300 0.009 0.000 1.6 0.1 300<		S1	36.50° S 13.10° E	4915	20	0.038	0.002	5.5	0.3
40 0.099 0.005 nd 70 0.107 0.005 nd 300 0.112 0.006 nd 500 0.007 0.005 nd 700 0.091 0.005 nd 700 0.091 0.005 nd 700 0.091 0.005 nd 1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 300 0.0					30	0.039	0.002	5.5	0.4
70 0.107 0.005 nd 300 0.112 0.006 nd 500 0.007 0.005 nd 700 0.091 0.005 nd 1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.099 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3050 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 350 0.009 0.000 1.5 0.2 95 0.040 0.00					40	0.099	0.005	nd	
300 0.112 0.006 nd 500 0.107 0.005 nd 700 0.091 0.005 nd 1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.0 4000 0.010 0.000 0.66 0.0 4000 0.010 0.000 0.6 0.0 1.2 41.18°S 09.92°E 4525 15 0.040 0.002 25.4 1.3 35 0.009 0.000 nd 45 0.009 0.000 nd 45 0.009 0.000 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.022 0.001 2.0 0.2					70	0.107	0.005	nd	
500 0.107 0.005 nd 700 0.091 0.005 nd 1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 0.6 0.0 4000 0.010 0.000 0.6 0.0 445 0.009 0.000 1.5 0.2 95 0.094 0.005 3.1 300 0.102 0.001 2.3 0.2 1200 0.025 0.01					300	0.112	0.006	nd	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					500	0.107	0.005	nd	
1000 0.039 0.002 3.9 0.3 1200 0.029 0.001 3.1 0.2 1400 0.015 0.001 2.0 0.1 1600 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.3 0.3 2000 0.009 0.000 1.4 0.1 3050 0.009 0.000 1.6 0.1 3500 0.009 0.000 1.6 0.1 3800 0.009 0.000 1.6 0.1 3800 0.009 0.000 0.8 0.0 4000 0.010 0.000 0.8 0.0 4000 0.010 0.000 0.6 0.0 4000 0.010 0.000 0.6 0.0 4000 0.010 0.000 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2					700	0.091	0.005	nd	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					1000	0.039	0.002	3.9	0.3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					1200	0.029	0.001	3.1	0.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					1400	0.015	0.001	2.0	0.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					1600	0.009	0.000	1.3 mal	0.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					2000	0.009	0.000	14	0.1
L2 41.18°S 09.92°E 4525 15 0.009 0.000 1.6 0.1 3500 0.009 0.000 0.8 0.0 4000 0.010 0.000 0.8 0.0 4000 0.010 0.000 0.6 0.0 4000 0.010 0.000 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					2700	0.009	0.000	1.4	0.1
L2 41.18°S 09.92°E 4525 15 0.040 0.009 0.000 0.8 0.0 4000 0.010 0.000 0.8 0.0 4000 0.010 0.000 0.6 0.0 4000 0.010 0.000 0.6 0.0 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					2500	0.009	0.000	1.0	0.0
4000 0.010 0.000 0.6 0.0 4000 0.010 0.000 0.6 0.0 L2 41.18°S 09.92°E 4525 15 0.040 0.002 25.4 1.3 35 0.009 0.000 nd 45 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					3800	0.009	0.000	0.80	0.1
L2 41.18°S 09.92°E 4525 15 0.040 0.002 25.4 1.3 35 0.009 0.000 nd 45 0.009 0.000 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					4000	0.000	0.000	0.0 0.0	0.0
L2 41.10 0.00.21 40.20 100 0.000 0.000 nd 35 0.009 0.000 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1		12	41 18° S 09 92° F	4525	+000	0.010	0.000	25.4	13
45 0.009 0.000 1.5 0.2 95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1			11.10 0 00.02 E	1020	35	0.009	0.000	nd	1.0
95 0.094 0.005 32.3 3.1 300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					45	0.009	0.000	1.5	02
300 0.102 0.005 nd 600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					95	0.094	0.005	32.3	3.1
600 0.047 0.002 6.4 0.4 800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.001 1.0 0.1					300	0.102	0.005	nd	
800 0.025 0.001 2.3 0.2 1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					600	0.047	0.002	6.4	0.4
1200 0.022 0.001 2.7 0.2 1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					800	0.025	0.001	2.3	0.2
1400 0.015 0.001 2.0 0.2 2100 0.009 0.000 1.0 0.1					1200	0.022	0.001	2.7	0.2
2100 0.009 0.000 1.0 0.1					1400	0.015	0.001	2.0	0.2
					2100	0.009	0.000	1.0	0.1

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Table 2	. Continued
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Domain	Station	Position	Bottom depth (m)	Depth (m)	Fe(II) (nM)	STD (nM)	Fe(II)/DFe (%)	STD (%)
ACC	S2	42.47° S 08.93° E	4070	15	0.024	0.001	13.3	1.6
				30	0.019	0.001	14.6	2.1
				35	0.021	0.001	21.5	2.8
				45	0.116	0.006	nd	
				196	0.125	0.007	70.4	5.8
				314	0.105	0.006	62.3	4.9
				461	0.102	0.006	nd	
				598	0.093	0.005	nd	
				809	0.088	0.005	20.2	1.3
				1029	0.078	0.004	18.0	1.3
				1250	0.071	0.004	15.5	1.1
				1441	0.051	0.003	7.9	0.5
				1764	0.032	0.002	5.0	0.3
				2156	0.033	0.002	3.2	0.2
				2548	0.027	0.001	3.4	0.2
				2891	0.020	0.001	1.4	0.1
				3234	0.025	0.001	3.2	0.3
				3626	0.020	0.001	2.8	0.2
				3940	0.023	0.001	3.7	0.2
	L3	44.88° S, 06.88° E	4315	30	0.043	0.003	nd	
				100	0.019	0.002	9.3	1.7
				150	0.017	0.002	14.4	2.7
				270	0.023	0.002	11.6	1.4
				400	0.016	0.002	4.7	0.7
				600	0.013	0.001	3.1	0.4
				1200	0.009	0.001	0.9	0.1
				1400	0.009	0.001	1.1	0.1
				2100	0.011	0.001	1.8	0.2
	L4	46.02° S 05.87° E	4147	30	0.035	0.002	21.0	3.2
				60	0.030	0.002	nd	
				100	0.046	0.002	22.3	2.3
				150	0.023	0.001	10.1	1.1
				270	0.029	0.001	10.4	0.7
				480	0.024	0.001	6.3	0.7
				800	0.018	0.001	5.3	0.3
				1600	0.018	0.001	2.5	0.2
				2050	0.016	0.001	2.1	0.2
	S3	47.55° S 04.37° E	4480	20	0.065	0.003	40.2	7.0
				30	0.066	0.003	38.7	2.8
				40	0.032	0.002	nd	
				70	0.021	0.001	11.5	1.4
				100	0.018	0.001	9.6	1.6
				200	0.048	0.002	33.8	3.9
				300	0.063	0.003	22.6	1.4
				450	0.055	0.003	19.1	1.0
				600	0.050	0.002	12.2	0.9
				800	0.041	0.002	7.3	0.5
				10/0	0.037	0.002	5.6	0.4
				1500	0.028	0.001	4.6	0.3
				2020	0.018	0.001	1.6	0.1



Table 2.	Continued.
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L5 49.03° S 02.84° E 4025 L5 40 0.018 0.001 L5 40.065 L5 40.0087 L5 40.0087 L5 40.0087 L6 50.38° S 01.33° E 3576 L6 50.011 32 L6 50.38° S 01.33° E 3576 L6 50.011 44 L7 55.23° S 00.03° E 2632 L6 50.001 10 0.001 L7 55.23° S 00.03° E 2770 L7 55.23° S 00.	Domain	Station	Position	Bottom depth (m)	Depth (m)	Fe(II) (nM)	STD (nM)	Fe(II)/DFe	STD (%)
L5 49.03°S 02.84°E 4025 49.03°S 02.84°E 4025 40.018 0.001 12.6 1.4 3980 0.010 0.001 12.6 1.4 80 0.065 0.002 49.2 1.7 150 0.065 0.002 49.2 1.7 170 0.867 0.002 nd 250 0.055 0.002 25.6 1.2 350 0.048 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 L6 50.38°S 01.33°E 3576 30 0.039 0.002 15.8 1.8 60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 4.3 1.0 60 0.014 0.001 1.6 0.1 800 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 800 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 2100 0.011 0.001 9.6 1.5 135 0.015 0.001 4.4 1.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 2100 0.011 0.001 1.6 0.1 850 0.026 0.003 5.6 4.9 180 0.064 0.003 5.6 4.9 180 0.064 0.003 29.4 1.8 200 0.035 0.002 21.9 1600 0.004 0.003 29.4 1.8 200 0.035 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.006 0.003 24.9 2.7 350 0.006 0.003 24.9 1.6 500 0.057 0.003 24.9 2.7 350 0.006 0.003 24.4 1.8 200 0.037 0.002 1.1 0.1 100 0.017 0.001 1.6 0.0 110 1 2000 0.012 0.001 1.4.6 1.0 100 0.012 0.001 1.4.6 1.0 110 0.017 0.001 2.6.1 2.4 200 0.037 0.002 1.7.4 1.1 300 0.031 0.002 8.3 0.5 100 0.019 0.001 4.0 0.3 1000 0.012 0.001 4.0					2500	0.015	0.001	1.0	0.0
L5 49.03°S 02.84°E 4025 49.03°S 02.84°E 4025 40 0.018 0.001 12.6 1.4 80 0.060 0.001 12.6 1.4 80 0.065 0.002 49.2 1.7 170 0.087 0.002 nd 250 0.055 0.002 25.6 1.2 350 0.048 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.039 0.003 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 L6 50.38°S 01.33°E 3576 30 0.039 0.002 15.8 1.8 60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 4.3 1.0 60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.016 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 1850 0.018 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 1850 0.010 0.000 2.3 0.2 2100 0.011 0.001 2.8 0.2 1600 0.010 1.001 1.0 0.1 S4 51.85°S 00.00°E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.003 44.4 4.8 160 0.064 0.003 50.6 4.9 180 0.054 0.003 24.9 2.7 350 0.000 0.03 44.4 4.8 160 0.064 0.003 50.6 4.9 180 0.054 0.003 24.9 2.7 350 0.000 0.03 24.9 2.7 350 0.000 0.003 24.9 2.7 350 0.000 0.001 14.6 1.0 400 0.047 0.000 2.8 3 0.5 500 0.003 24.9 2.7 350 0.000 0.003 24.9 2.7 350 0.000 0.001 14.6 1.0 400 0.047 0.000 2.8 3 0.5 500 0.003 24.9 2.7 350 0.000 0.001 14.6 1.0 400 0.017 0.001 26.0 3.7 100 0.017 0.001 26.0 3.7 100 0.017 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1000 0.019 0.001 4.5 0.2 1000 0.019 0.001 4.5 0.2 1000 0.019 0.001 4.5 0.2					2000	0.015	0.001	1.9	0.2
L5 49.03°S 02.84°E 4025 40 0.018 0.001 12.6 1.4 80 0.060 0.001 nd 150 0.065 0.002 49.2 1.7 170 0.087 0.002 nd 120 0.055 0.002 25.6 1.2 350 0.048 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.026 0.003 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 L6 50.38°S 01.33°E 3576 30 0.039 0.002 15.8 1.8 60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 4.3 1.0 60 0.014 0.001 1.6 0.1 850 0.012 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 2100 0.011 0.001 1.0 0.1 S4 51.85°S 00.00°E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.004 nd 130 0.064 0.003 29.4 1.8 250 0.066 0.003 29.4 1.8 250 0.066 0.003 29.4 1.8 250 0.066 0.003 34.5 2.6 300 0.035 0.003 29.4 1.8 250 0.066 0.003 34.5 2.6 300 0.054 0.003 29.4 1.8 250 0.066 0.003 34.5 2.6 300 0.054 0.003 29.4 1.8 250 0.066 0.003 29.4 1.8 250 0.060 0.003 29.6 1.9 400 0.047 0.002 21.9 1.6 500 0.071 0.001 1.4.6 1.0 100 0.012 0.001 1.4.6 1.0 110 0.017 0.001 26.0 3.7 120 0.024 0.001 1.6.6 0.3 1950 0.020 0.001 1.4.6 1.0 100 0.012 0.001 1.4.6 1.0 100 0.012 0.001 26.1 2.4 200 0.037 0.002 8.3 0.5 900 0.049 0.002 8.3 0.5 900 0.049 0.002 8.3 0.5 900 0.049 0.002 8.3 0.5 900 0.049 0.002 1.4.5 0.2 1000 0.012 0.001 26.1 2.4 200 0.037 0.002 8.3 0.5 900 0.041 0.001 1.6.6 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 8.3 0.5 900 0.001 0.14.5 0.2 1000 0.012 0.001 4.5 0.2 1000 0.012 0.001 4.5 0.2 1000 0.019					3500	0.010	0.001	1.7	0.1
L5 49.03° S 02.84° E 4025 40 0.018 0.001 12.6 1.4 80 0.060 0.001 12.6 1.4 80 0.060 0.001 12.6 1.4 150 0.065 0.002 49.2 1.7 170 0.087 0.002 nd 250 0.055 0.002 25.6 1.2 350 0.048 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.039 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 L6 50.38° S 01.33° E 3576 30 0.039 0.002 15.8 1.8 2200 0.023 0.001 3.2 0.2 L6 50.38° S 01.33° E 3576 30 0.039 0.002 15.8 1.8 135 0.015 0.001 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 nd 100 0.014 0.011 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.014 0.001 1.8 4 0.8 300 0.018 0.001 4.4 0.8 300 0.018 0.001 8.4 0.8 300 0.018 0.001 4.4 1.8 160 0.010 0.003 29.4 1.8 250 0.066 0.003 34.5 2.6 300 0.050 0.003 24.9 2.7 350 0.060 0.003 29.4 1.8 250 0.062 0.003 34.5 2.6 300 0.050 0.003 29.4 1.8 250 0.062 0.003 34.5 2.6 300 0.050 0.003 29.4 1.8 250 0.060 0.003 34.5 2.6 300 0.050 0.003 29.4 1.8 250 0.005 0.001 1.4 0.1 1.10 0.11 1.01 1.01 1.01 1.01 1.01 1.01 1.00 0.17 0.001 2.6.0 3.7 120 0.021 0.001 1.4 0.0 3.7 120 0.024 0.001 2.6.1 2.4 200 0.037 0.002 1.4 0.0 3.5 5.5 5.5 5.5 5.5 5.5 5.5 5.5					3080	0.009	0.000	1.2	0.1
L6		15	40.03° S 02.84° E	4025	3900	0.010	0.001	12.6	1 /
150 0.005 0.002 49.2 1.7 170 0.087 0.002 nd 250 0.055 0.002 25.6 1.2 250 0.035 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.039 0.003 7.7 0.7 71600 0.022 0.023 1.5 8.8 2200 0.023 0.001 3.2 0.2 1.6 1.5 1.35 0.15 0.001 nd 1.5 135 0.018 0.001 1.6 1.1 1.6 1.5 1.35 0.011 1.6 1.1 1.5 1.35 0.012 0.001 1.6 1.1 1.1 1.1 1.6 1.5 1.35 0.012 0.01 1.4 1.0 1.5 1.35 0.01 1.4 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1		20	40.00 0 02.04 E	4020	80	0.060	0.001	nd	1.4
170 0.087 0.002 nd nd 250 0.055 0.002 25.6 1.2 350 0.048 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.039 0.003 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 100 0.021 0.001 3.2 0.2 100 0.021 0.001 3.6 1.4 100 0.021 0.001 3.6 1.5 135 0.015 0.001 1.6 0.1 180 0.018 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.6 0.1 350 0.060 0.003 24.4 4.8 160 0.060 0.003 24.9 1.7					150	0.065	0.002	49.2	17
L6 50.38°S 01.33°E 3576 30 0.02 25.6 1.2 350 0.048 0.003 13.6 1.4 700 0.039 0.003 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 2200 0.023 0.001 3.2 0.2 2200 0.021 0.001 9.6 1.5 135 0.015 0.001 d. 100 0.021 0.001 9.6 1.5 135 0.015 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.0 0.1 850 0.012 0.001 2.8 0.2 1600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 2100 0.011 0.001 1.0 0.1 180 0.064 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.666 0.003 34.5 2.6 300 0.054 0.003 29.4 1.8 250 0.666 0.003 34.5 2.6 300 0.054 0.003 29.4 1.8 250 0.666 0.003 34.5 2.6 300 0.057 0.003 12.8 0.7 700 0.035 0.002 11.8 0.7 700 0.035 0.002 1.8 0.7 700 0.035 0.002 1.8 0.7 700 0.035 0.002 1.8 0.7 700 0.035 0.002 1.9 400 0.047 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 1.9 400 0.047 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 1.1 0.1 117 0.266 0.001 5.6 0.3 1950 0.021 0.001 1.4 0.1 100 0.017 0.01 28.0 3.7 700 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.014 0.001 5.6 0.3 1500 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.001 0.001 2.5 0.2 1500 0.011 0.001 1.4 0.03					170	0.087	0.002	nd	
350 0.048 0.003 13.6 1.4 700 0.036 0.004 6.0 1.0 1000 0.039 0.003 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 160 0.024 0.002 nd 1.5 135 0.018 0.001 9.6 1.5 135 0.018 0.001 8.4 0.8 300 0.018 0.001 8.4 0.8 300 0.018 0.001 8.4 0.8 300 0.018 0.001 2.8 0.2 1600 0.010 0.001 1.6 0.1 850 0.022 0.011 0.001 1.8 0.2 1600 0.010 0.001 1.0 0.1 0.1 130 0.066 0.003 34.4 4.8 160 0.064 0.003 <td></td> <td></td> <td></td> <td></td> <td>250</td> <td>0.055</td> <td>0.002</td> <td>25.6</td> <td>1.2</td>					250	0.055	0.002	25.6	1.2
700 0.036 0.004 6.0 1.0 1000 0.039 0.003 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 100 0.021 0.001 3.2 0.2 100 0.021 0.001 3.4 0.8 100 0.021 0.001 9.6 1.5 135 0.015 0.001 nd 1.6 180 0.018 0.001 2.8 0.2 1600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.014 0.001 1.6 0.1 850 0.012 0.011 1.0 1.0 100 0.060 0.003 2.4 4.8 160 0.664 0.003 2.4 1.8 250 0.666 0.003 2.4 2.7					350	0.048	0.003	13.6	14
L6 50.38°S 01.33°E 3576 30 0.03 7.7 0.7 1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 0.023 0.002 15.8 1.8 60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 nd 180 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.0 0.1 854 51.85°S 00.00°E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.003 4.4 4.8 160 0.064 0.003 50.6 4.9 180 0.054 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.021 0.001 14.6 1.0 400 0.47 0.002 8.3 0.5 900 0.44 0.001 2.6 0.3 150 0.021 0.001 14.6 1.0 100 0.017 0.001 2.6 0.3 150 0.021 0.001 14.6 1.0 160 0.012 0.001 14.6 1.0 160 0.012 0.001 14.6 1.0 160 0.012 0.001 14.6 1.0 160 0.012 0.001 2.5 0.2 1500 0.001 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.0					700	0.036	0.004	6.0	1.0
1600 0.026 0.003 5.5 0.8 2200 0.023 0.001 3.2 0.2 100 0.021 0.001 15.8 1.8 100 0.021 0.001 9.6 1.5 135 0.015 0.001 9.6 1.5 135 0.015 0.001 9.6 1.5 135 0.015 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 800 0.012 0.001 2.8 0.2 1600 0.010 0.001 1.0 0.1 84 51.85°S 00.00°E 2632 30 0.116 0.004 nd 130 0.066 0.003 50.6 4.9 180 0.054 0.003 24.9 1.6 500 0.057 0.003 24.9 2.7 350 0.060 0.03 <td< td=""><td></td><td></td><td></td><td></td><td>1000</td><td>0.039</td><td>0.003</td><td>7.7</td><td>0.7</td></td<>					1000	0.039	0.003	7.7	0.7
L6 50.38°S 01.33°E 3576 30 0.039 0.002 115.8 1.8 100 0.021 0.001 9.6 1.5 135 0.015 0.001 9.6 1.5 135 0.015 0.001 9.6 1.5 135 0.015 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 2.8 0.2 1600 0.011 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.6 0.1 54 51.85° S 00.00° E 2632 30 0.116 0.006 63.5 4.6 100 0.660 0.003 24.4 4.8 160 0.664 0.003 2.4 1.8 250 0.666 0.003 2.49 1.7 355 0.002 8.3 0.5 900 <td></td> <td></td> <td></td> <td></td> <td>1600</td> <td>0.026</td> <td>0.003</td> <td>5.5</td> <td>0.8</td>					1600	0.026	0.003	5.5	0.8
L6 50.38°S 01.33°E 3576 30 0.039 0.002 15.8 1.8 60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 nd 180 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 800 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.0 0.1 84 51.85°S 00.00°E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.003 44.4 4.8 160 0.064 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.066 0.003 34.5 2.6 300 0.050 0.003 24.9 2.7 350 0.066 0.003 24.9 2.7 350 0.066 0.003 24.9 2.7 350 0.066 0.003 29.4 1.8 250 0.066 0.003 29.4 1.8 250 0.066 0.003 29.4 1.8 250 0.066 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 350 0.066 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.000 0.01 1.0 1 4.5 0.2 1500 0.001 0.001 14.6 1.0 300 0.012 0.001 14.6 1.0 300 0.331 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 3500 0.014 0.0					2200	0.023	0.001	3.2	0.2
60 0.047 0.002 nd 100 0.021 0.001 9.6 1.5 135 0.015 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.001 1.0 0.1 850 0.012 0.001 1.0 0.1 100 0.010 0.001 1.0 0.1 100 0.011 0.001 1.0 0.1 1100 0.011 0.001 1.0 0.1 130 0.060 0.003 4.4 4.8 160 0.064 0.003 29.4 1.8 180 0.054 0.003 29.4 1.8 250 0.060 0.003 29.6 1.9		L6	50.38° S 01.33° E	3576	30	0.039	0.002	15.8	1.8
100 0.021 0.001 9.6 1.5 135 0.015 0.001 nd					60	0.047	0.002	nd	
135 0.015 0.001 nd 180 0.018 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.0 0.1 54 51.85° S 00.00° E 2632 30 0.116 0.006 663.5 4.6 600 0.064 0.003 44.4 4.8 160 0.064 0.003 29.4 1.8 250 0.666 0.003 24.5 2.6 300 0.050 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.002 1.9 400 <td></td> <td></td> <td></td> <td></td> <td>100</td> <td>0.021</td> <td>0.001</td> <td>9.6</td> <td>1.5</td>					100	0.021	0.001	9.6	1.5
180 0.018 0.001 8.4 0.8 300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.001 2.8 0.2 2100 0.011 0.00 2.3 0.2 2100 0.011 0.00 4.3 1.0 54 51.85° S 00.00° E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.004 nd nd 130 0.606 0.003 24.4 4.8 160 0.064 0.003 34.5 2.6 300 0.050 0.003 24.9 2.7 350 0.660 0.003 24.8 0.7 700 0.355 0.002 8.0 900 0.404 0.001 5.6 0.3 1117 0.026 0.01 1.6 500					135	0.015	0.001	nd	
300 0.018 0.001 4.3 1.0 600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 1600 0.011 0.001 1.0 0.1 S4 51.85° S 00.00° E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.004 nd 10 100 10 10 130 0.060 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.066 0.003 24.4 1.8 260 0.060 0.003 29.6 1.9 400 0.047 0.002 21.9 1.6 500 0.003 1.8 0.7 700 0.035 0.002 8.3 0.5 900 0.011 1.0 1.0 2500 0.009 0.11 <t< td=""><td></td><td></td><td></td><td></td><td>180</td><td>0.018</td><td>0.001</td><td>8.4</td><td>0.8</td></t<>					180	0.018	0.001	8.4	0.8
600 0.014 0.001 1.6 0.1 850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.000 2.3 0.2 2100 0.011 0.006 63.5 4.6 60 0.81 0.004 nd 130 0.060 0.003 44.4 4.8 160 0.064 0.003 29.4 1.8 250 0.066 0.003 24.4 2.6 300 0.050 0.003 24.9 2.7 350 0.660 0.003 24.6 1.6 500 0.057 0.003 24.8 0.7 700 0.35 0.002 8.3 0.5 900 0.049 0.002 nd 1117 200 0.012 0.001 nd 200 200 0.021 0.001 nd 1.01					300	0.018	0.001	4.3	1.0
850 0.012 0.001 2.8 0.2 1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.0 0.1 S4 51.85° S 00.00° E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.003 44.4 4.8 160 0.064 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 29.6 1.9 400 0.047 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.494 0.001 5.6 0.3 1117 0.26 0.001 5.6 0.3 1950 0.221 0.001 nd 2300 0.012 0.001 1.6 1.0 100 0.1					600	0.014	0.001	1.6	0.1
1600 0.010 0.000 2.3 0.2 2100 0.011 0.001 1.0 0.1 S4 51.85°S 00.00°E 2632 30 0.116 0.006 63.5 4.6 130 0.066 0.003 54.6 4.8 1600 0.664 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 350 0.660 0.003 29.6 1.9 400 0.047 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 nd 1117 1117 0.026 0.011 nd 1.01 2500 0.012 0.001 1.6 1.0 100 0.017 0.020 8.3 0.5 900 0.024 0.001 1.6 1.0 1117 0.2523°S 00.03°E					850	0.012	0.001	2.8	0.2
2100 0.011 0.001 1.0 0.1 S4 51.85°S 00.00°E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.004 nd 130 0.066 0.003 44.4 4.8 160 0.664 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 350 0.005 0.003 24.9 2.7 350 0.005 0.003 24.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 nd 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2200 0.012 0.001 nd 2200 0.009 0.000 1.1 0.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 2.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.011 0.001 4.5 0.2					1600	0.010	0.000	2.3	0.2
S4 51.85° S 00.00° E 2632 30 0.116 0.006 63.5 4.6 60 0.081 0.004 nd 130 0.060 0.003 44.4 4.8 160 0.054 0.003 24.4 4.8 160 0.054 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 12.8 0.7 700 0.335 0.002 8.3 0.5 900 0.049 0.002 nd 1117 1117 0.026 0.001 nd 2300 2500 0.009 0.000 1.1 0.1 2500 0.012 0.001					2100	0.011	0.001	1.0	0.1
60 0.081 0.003 44.4 4.8 130 0.660 0.003 45.4 4.8 160 0.064 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 300 0.050 0.003 24.9 2.7 350 0.060 0.003 29.6 1.9 400 0.047 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.001 5.6 0.3 1117 0.026 0.001 16.6 0.3 1117 0.021 0.001 nd 2500 0.001 1.0 2000 0.012 0.001 14.6 1.0 1.0 1.0 210 0.012 0.001 18.7 2.1 1.0 1.0 100 0.017 0.001 26.0 3.7 120		S4	51.85° S 00.00° E	2632	30	0.116	0.006	63.5	4.6
130 0.060 0.003 44.4 4.8 160 0.064 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.066 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.067 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 8.3 0.5 900 0.049 0.002 8.3 0.5 900 0.049 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2300 0.012 0.001 14.6 1.0 60 0.012 0.001 14.6 1.0 100 0.017 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.2 1500 0.011 2.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.0 0.3 1500 0.011 0.001 4.0 0.3 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.0 0.3 1500 0.011 0.001 4.0 0.3 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.0 0.3 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.5 0.2 1500 0.011 0.001 4.0 0.3 1500 0.011 0.001 0.001 0.001 0.00					60	0.081	0.004	nd	
160 0.064 0.003 50.6 4.9 180 0.054 0.003 29.4 1.8 250 0.066 0.003 34.5 2.6 300 0.050 0.003 24.9 2.7 350 0.060 0.003 29.6 1.9 400 0.047 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 nd 1117 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 1.01 1.01 1.01 L7 55.23° S 00.03° E 2770 30 0.016 0.001 18.7 2.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002					130	0.060	0.003	44.4	4.8
L7 55.23°S 00.03°E 2770 30 0.012 0.001 26.1 2.4 L7 55.23°S 00.03°E 2770 30 0.012 0.001 18.7 2.1 100 0.017 0.001 26.1 2.4 110 0.017 0.001 26.1 2.4 110 0.017 0.001 18.7 2.1 100 0.017 0.001 26.1 2.4 110 0.017 0.01 26.0 3.7 120 0.024 0.001 26.1 2.4 120 0.024 0.001 26.1 2.4 120 0.024 0.001 26.1 2.4 120 0.037 0.002 17.4 1.1 300 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.014 0.001 4.6 0.3 1500 0.012 0.001 4.5 0.2 1500 0.014 0.001 4.6 0.3 1500 0.012 0.001 4.5 0.2 1500 0.014 0.001 4.6 0.3 1500 0.012 0.001 4.5 0.2 1500 0.014 0.001 4.5 0.2 1500 0.014 0.001 4.0 0.3 1500 0.014 0.001 4.0 0.3					160	0.064	0.003	50.6	4.9
L7 55.23°S 00.03°E 2770 30 0.012 0.001 26.1 2.4 2300 0.050 0.003 24.9 2.7 350 0.060 0.003 24.9 2.7 350 0.067 0.003 24.9 2.7 350 0.067 0.003 24.9 2.7 350 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 nd 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 2.5 0.2 1500 0.012 0.001 4.0 0.3					180	0.054	0.003	29.4	1.8
L7 55.23°S 00.03°E 2770 L7 55.23°S 00.03°E 27					250	0.066	0.003	34.5	2.6
L7 55.23°S 00.03°E 2770 30 0.016 0.001 26.0 3.7 120 0.037 0.002 21.9 1.6 500 0.057 0.003 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 nd 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.012 0.001 4.5 0.2 1500 0.019 0.001 4.5 0.2 1500 0.019 0.001 4.0 0.3					300	0.050	0.003	24.9	2.7
L7 55.23°S 00.03°E 2770 30 0.012 0.001 26.1 2.4 100 0.047 0.002 12.8 0.7 700 0.035 0.002 8.3 0.5 900 0.049 0.002 nd 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 0.001 14.6 1.0 60 0.012 0.001 14.6 1.0 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.0 0.3					350	0.060	0.003	29.6	1.9
L7 55.23°S 00.03°E 2770 30 0.0157 0.002 8.3 0.5 900 0.049 0.002 8.3 0.5 900 0.049 0.002 nd 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 100 0.016 0.001 14.6 1.0 60 0.012 0.001 14.6 1.0 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.37 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 4.5 0.2 1500 0.012 0.001 4.0 0.3					400	0.047	0.002	21.9	1.6
L7 55.23° S 00.03° E 2770 30 0.014 0.001 4.5 0.2 120 0.037 0.002 nd 1117 0.026 0.001 5.6 0.3 1950 0.021 0.001 nd 2300 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 0.016 0.001 14.6 1.0 60 0.012 0.001 18.7 2.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.31 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 2.5 0.2 1500 0.019 0.001 4.0 0.3					500	0.057	0.003	12.8	0.7
L7 55.23°S 00.03°E 2770 30 0.012 0.001 18.7 2.1 100 0.012 0.001 14.6 1.0 2500 0.012 0.001 14.6 1.0 0.017 0.001 26.0 3.7 120 0.024 0.001 26.0 3.7 120 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 2.5 0.2 1500 0.013 0.001 4.0 0.3					700	0.035	0.002	8.3	0.5
L7 55.23°S 00.03°E 2770 30 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 60 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 60 0.012 0.001 14.6 1.0 60 0.012 0.001 18.7 2.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 2.5 0.2 1500 0.019 0.001 4.0 0.3					900	0.049	0.002	na 5.6	0.2
L7 55.23°S 00.03°E 2770 30 0.012 0.001 nd 2500 0.009 0.000 1.1 0.1 L7 55.23°S 00.03°E 2770 30 0.016 0.001 14.6 1.0 60 0.012 0.001 18.7 2.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 4.0 0.3					1050	0.020	0.001	5.0 nd	0.5
2500 0.009 0.000 1.1 0.1 L7 55.23°S 00.03°E 2770 30 0.016 0.001 14.6 1.0 60 0.012 0.001 18.7 2.1 100 0.017 0.001 22.0 3.7 120 0.024 0.001 22.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.019 0.001 4.0 0.3					2300	0.021	0.001	nd	
L7 55.23°S 00.03°E 2770 30 0.016 0.001 14.6 1.0 60 0.012 0.001 14.6 1.0 60 0.012 0.001 18.7 2.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1500 0.012 0.001 4.0 0.3					2500	0.012	0.001	11	0.1
60 0.012 0.001 18.7 2.1 60 0.012 0.001 18.7 2.1 100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1000 0.012 0.001 2.5 0.2 1500 0.019 0.001 4.0 0.3		17	55 23° S 00 03° E	2770	2000	0.009	0.000	14.6	1.0
100 0.017 0.001 26.0 3.7 120 0.024 0.001 26.1 3.7 120 0.024 0.001 26.1 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1000 0.012 0.001 2.5 0.2 1500 0.012 0.001 4.0 0.3		-/	33.20 0 00.00 L	2110	60	0.012	0.001	18.7	21
100 0.024 0.001 26.5 2.4 200 0.037 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1000 0.012 0.001 2.5 0.2 1500 0.019 0.001 4.0 0.3					100	0.012	0.001	26.0	37
120 0.027 0.002 17.4 1.1 300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1000 0.012 0.001 2.5 0.2 1500 0.012 0.001 4.0 0.3					120	0.024	0.001	26.1	24
300 0.031 0.002 8.3 0.5 650 0.020 0.001 4.5 0.2 1000 0.012 0.001 2.5 0.2 1500 0.012 0.001 4.0 0.3					200	0.037	0.002	17.4	1.1
650 0.020 0.001 4.5 0.2 1000 0.012 0.001 2.5 0.2 1500 0.019 0.001 4.0 0.3					300	0.031	0.002	8.3	0.5
1000 0.012 0.001 2.5 0.2 1500 0.019 0.001 4.0 0.3					650	0.020	0.001	4.5	0.2
1500 0.019 0.001 4.0 0.3					1000	0.012	0.001	2.5	0.2
					1500	0.019	0.001	4.0	0.3



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Table 2. Continued.

Domain	Station	Position	Bottom depth (m)	Depth (m)	Fe(II) (nM)	STD (nM)	Fe(II)/DFe (%)	STD (%)
EWSG	S5	57.55° S 00.03° W	3932	30	0.063	0.003	66.6	8.4
				60	0.042	0.002	44.4	2.5
				120	0.017	0.001	8.3	0.6
				140	0.018	0.001	24.4	3.4
				190	0.014	0.001	16.0	1.0
				250	0.025	0.001	22.5	1.8
				350	0.011	0.001	11.8	0.7
				550	0.014	0.001	12.9	1.0
				750	0.021	0.001	4.4	0.5
				800	0.024	0.001	7.1	0.5
				1250	0.009	0.000	2.2	0.1
				1700	0.009	0.000	3.5	0.2
				2150	0.035	0.002	12.2	0.7
				2600	0.036	0.002	10.0	0.9
				3050	0.047	0.002	11.2	0.6
				3500	0.050	0.003	13.1	0.8
				3840	0.044	0.002	8.5	0.8

Table 3. Theoretical values of Fe(II) half lifes (in min) for surface and deep water samples at 4 °C using models of Fe(II) oxidation kinetics (Santana-Casiano et al., 2005: Model I; Trapp and Millero, 2007: Model II; see Supplement). The ionic strength has been calculated from salinity using the equation I = (19.9201 s)/(1000 - 1.00488 s) (Millero, 1995).

	Theoretical values						Measured		
Stations	Latitude (° S)	I(M)	[O ₂]	[H ₂ O ₂]	pН	$[CO_{3}^{2-}]$	Model I	Model II	values
		. ,	(µM)	(nM)	-	(μΜ)	t1/2 (min)	<i>t</i> 1/2 (min)	t1/2 (min)
Upper waters									
L1	34.43	0.74	233.7	27.0	8.09	216.1	7.5	5.5	2.9
S1	36.50	0.73	245.4	19.6	8.12	209.1	7.7	5.6	2.9
L2	41.18	0.71	251.3	2.4	7.99	110.3	18.4	13.6	3.8
S2	42.47	0.71	273.5	2.1	8.04	117.9	15.4	11.4	7.6
L3	44.88	0.70	293.2		8.07	128.0	12.6	9.7	6.4
L4	46.02	0.70	300.9	21.5	8.07	125.0	11.3	9.0	6.2
S3	47.55	0.70	311.3	15.1	8.08	119.8	12.0	9.4	9.0
L5	49.03	0.70	313.5	19.8	8.07	120.0	11.6	9.2	8.3
L6	50.38	0.70	326.2	22.6	8.08	112.1	12.2	9.6	5.9
S4	51.85	0.69	340.7	9.0	8.05	106.1	13.4	10.4	8.8
L7	55.23	0.70	349.2	31.1	8.06	98.8	13.1	10.3	7.0
S5	57.55	0.70	353.3	31.5	8.06	93.9	14.1	10.9	11.3
Deep waters									
S1	36.50	0.72	218.0		7.93	90.5	91.1	20.4	43.8
L2	41.18	0.71	187.7	1.1	7.85	74.6	127.0	30.8	63.4
S2	42.47	0.71	185.4		7.86	75.3	132.6	31.0	11.8
S2	42.47	0.72	227.8		7.88	91.3	85.6	19.2	14.6
L3	44.88	0.71	185.5		7.85	76.2	130.5	30.5	10.0
L4	46.02	0.72	187.0		7.87	85.5	114.8	26.1	39.2
S3	47.55	0.71	181.2		7.86	74.5	137.6	32.3	36.7
S3	47.55	0.72	218.7		7.84	81.7	101.3	23.3	37.6
L5	49.03	0.71	180.5	1.4	7.85	77.6	125.5	30.3	28.2
S4	51.85	0.71	183.9		7.88	79.5	126.7	29.2	33.6
S4	51.85	0.72	218.5		7.87	84.0	98.8	22.6	40.5
L7	55.23	0.72	201.9	6.3	7.92	84.4	89.9	23.4	30.9
S5	57.55	0.72	209.1		7.91	76.8	115.8	26.8	72.3
S5	57.55	0.72	252.4		7.85	79.7	89.8	20.8	47.2



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Table 4. Fe(II) concentration ranges in previous published studies.

Latitude/ Longitude	Environments/ Experiments	Depth range (m)	[Fe(II)] range	Reference
33.43° S–57.55° S/14.40° E– 00.03° W	Open Ocean South Atlantic/Southern Ocean	15–4000 m	9–125 pM	This study
30° N/135° E–118° W 14° S–56° N/152° W	Open Ocean Pacific Ocean and northern Philippine Sea	13–1010 m	<12–280 pM <12–76 pM	Hansard et al. (2009)
3.0° S–9.1° N/140° W	Open Ocean Equatorial Pacific	0–100 m	<120–530 pM	O'Sullivan et al.(1991)
178.72° E/46.24° S	Open Ocean, South West Pacific, FeCycle experiment.	2 m	Up to 46 pM (during night- time)	Croot et al. (2007)
23°18′S–24°48′S/8°39′E–	Open Ocean, South Atlantic	1–2 m	<12-45 pM	Bowie et al. (2002)
50°92′ S–51°25′ S/143°38′ E– 143°03′ E	Open Ocean, Southern Ocean, Subantarctic Front	1–2 m	<12–29 pM	Bowie et al. (2002)
42–51° N/23° E–2° W	Eastern North Atlantic, Euro- pean continental shelf and English Channel	2 m	<160 pM (oceanic waters) Up to 250 pM (shelf waters) 500–1800 pM (coastal wa- ters).	Boye et al. (2003)
37–42° N/23° W	Eastern North Atlantic	0–2000 m	<100–550 pM	Boye et al. (2006)
46° N–52.4° N/ 8° W–4.3° E	European continental margin. Open Ocean and shelf waters	3–4000 m	<12 → 200 pM	Ussher et al. (2007)
9.02° S–12.27° S/127.43° E– 144.19° E	Northern Australian shelf waters	2–3 m	Up to 3 nM	Waite et al. (1995)
31.53° N-h56.50° N/ 0.39° E–0.83° E	Northern North Sea	0–70m	Up to 1.2 nM	Gledhill and van den Berg (1995)
9.5° S–10.9° S/78.1° W–79.1° W	Suboxic zone, near the coast of Peru	0–2300 m	Up to 40 nM	Hong and Kester (1986)
17° N–23.5° N/ 57° E–74° E	Suboxic zone, Arabian Sea	0–1000 m	Up to 600 pM	Moffett et al. (2007)
15° N–18° N/ 105° W–115° W	Oxic-suboxic zone, Eastern Tropi- cal North Pacific	0–300 m	Up to 150 pM	Hopkison and Barbeau (2007)
61° S/140° E	Southern Ocean SOIREE fertiliza- tion experiment	2–3 m	Up to 1 nM	Croot et al. (2001)
48° S/21° E	Southern Ocean EISENEX fertil- ization experiment	0–100 m	Up to 1 nM	Croot and Laan (2002); Croot et al. (2005)
56.2° S-6-6° S/172° W	Southern Ocean SOFEX fertiliza- tion experiment	2–3 m	Up to 300 pM in patch	Croot et al. (2008)
50° S/2° E	Southern Ocean EIFEX fertiliza- tion experiment	2–3 m	Up to 800 pM in patch	Croot et al. (2008)
46.7° N/165.8° E	Sub-Arctic Pacific Ocean SEEDS II fertilization experiment	0–80 m	UP to > 200 pM in patch	Roy et al. (2008)



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Fig. 1. Location of the stations sampled during the BONUS-GoodHope cruise along with the three main oceanographic provinces encountered. The three domains crossed were the sub-tropical domain (stations L1, S1 and L2), the ACC domain (stations S2, L3, L4, S3, L5, L6, S4 and L7) and the eastern part of the Weddell Sea Gyre (station S5). Five fronts were crossed: the southern-subtropical front (S-STF), the sub Antarctic front (SAF), the polar front (PF), the southern ACC front (SACCF) and the southern boundary (Sbdy).





Fig. 2. Vertical distribution of salinity (a), theta (b), and oxygen (c) measured along the transect from the north (left) to the south (right) of the section. Water masses are indicated: AAIW: Antarctic Intermediate Water. This water mass is coming from the Indian Ocean through the Agulhas Current (I-AAIW) north of ~37° S and from the Atlantic sector (A-AAIW) south of 37° S (Gordon et al., 1992). NADW: North Atlantic Deep Water. The highest salinity values close to the African continental slope reflect advection by a southeastward deep boundary current (SE-NADW,Arhan et al., 2003). LCDW: Lower Circumpolar Deep Water and AABW: Antarctic Bottom Water.





(a)



(b)

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Fig. 3. Vertical section of (a) labile Fe(II) in nM and (b) %Fe(II)/DFe from the north (left) to the south (right) of the section. DFe data are from Chever et al. (2010).



Fig. 4. Natural logarithm transformation of the chemiluminescent integral vs. time for Fe(II) spikes (0.25–1 nM) in a surface sample **(a)** and a deep one **(b)**. See text for more details.











Fig. 6. Percentage of labile Fe(II) relative to dissolved Fe concentrations in the surface mixed layer for all the stations vs. the time at which sampling was done.





Fig. 7. Vertical profiles of 234 Th/ 238 U, labile Fe(II) and Baxs at station S2. Baxs is the biogenic particulate Ba calculated by subtracting the lithogenic Ba from total particulate Ba.





Fig. 8. Vertical profiles in the upper 1500 m of labile Fe(II) and *T* at the 4 stations south of the PF where the AAWW were clearly seen.

