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2 published version for accuracy and citation. Published in Marine Chemistry, 166, 25-35 (2014)
3 doi: 10.1016/j.marchem.2014.08.009.
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5 Determination of dissolved iron in seawater: A historical review

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15

16 Abstract

17

18 This paper overviews the evolution of suitable analytical approaches for the determination of
19 dissolved iron in seawater. The focus is on sampling and sample treatment, detection methods
20 and quality assurance of the data. Iron is a vital trace element for the growth of marine
21 organisms and is the limiting micronutrient for primary production in many parts of the world's
22 oceans. The concentration of dissolved iron in seawater therefore influences the past and
23 present day global carbon cycle and consequently Earth's climate. Hence it is important to
24 understand the marine biogeochemistry of iron and quantify the spatial and temporal distribution
25 of the element. In order to do this, it is essential that robust and validated methods with
26 appropriate detection limits, precision and accuracy are available for the determination of iron
27 species in seawater.

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29 Keywords: iron biogeochemistry; sampling; sample treatment; iron determination; data quality

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1. Iron biogeochemistry

Iron has a relative atomic mass of 55.847 a.m.u. and six known isotopes, of which ^{54}Fe (5.82 %), ^{56}Fe (91.66 %) and ^{57}Fe (2.19 %) are the most abundant (Taylor, 1964). The element has a high crustal abundance (~5.6 %) and its compounds make up a significant proportion of the Earth's rocks and soils but its low solubility dictates that dissolved iron concentrations in oceanic waters are typically sub-nanomolar (Liu and Millero, 2002). Iron exists predominantly as oxides and carbonates but forms salts with most inorganic anions in the solid phase. The most commonly occurring compounds in iron ores, all of which are highly stable, are haematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), siderite (FeCO_3) and pyrite (FeS_2) (Greenwood and Earnshaw, 1984).

The marine biogeochemistry of iron is influenced by low solubility, redox speciation and the role that it plays in biological cycles. The major inputs of iron to the oceans are from the atmosphere, continental shelf sediments, hydrothermal vents, rivers and glacial melt in polar regions. The main removal pathways are biological uptake, scavenging, precipitation and sedimentation. In the remote surface waters of the open-ocean (and some enclosed basins) the main source of iron is atmospheric dust deposition (Jickells and Spokes, 2001; Séguret et al., 2011). A summary of ambient dissolved iron concentrations in the major reservoirs and annual flux estimates between the reservoirs is shown in **Fig. 1** and an inventory of >13,000 oceanic dissolved iron measurements can be found in Tagliabue *et al.* (Tagliabue et al., 2012). Using the mean off-shelf dissolved iron concentrations (± 1 s.d.) from this inventory for surface (0 – 100 m) and deep (2000 – 6000 m) waters and a total ocean volume of $1.35 \times 10^9 \text{ km}^3$ gives estimates for standing stocks of dissolved iron of $2.34 \times 10^{13} \pm 3.40 \times 10^{13} \text{ g}$ for surface waters and $4.08 \times 10^{13} \pm 1.97 \times 10^{13} \text{ g}$ for deep waters.

In most oceanic regions, primary production is limited by the availability of light and macro-nutrients (nitrate, phosphate and silicate) but approximately 40 % of the world's surface waters are replete with major nutrients but have relatively low phytoplankton biomass (Boyd et al., 2007; Moore et al., 2002). These regions are termed high-nutrient, low chlorophyll (HNLC), the most important being the Southern Ocean, the Equatorial Pacific and the Subarctic Pacific. The first reliable iron determinations in an HNLC region were made in the late 1980's in the Pacific Ocean as part of the VERTEX programme (Landing and Bruland, 1987; Martin and Gordon, 1988; Martin et al., 1989) using sampling and analytical techniques developed by Bruland *et al.* (Bruland et al., 1979).

71 John Martin then published the 'Iron Hypothesis' in 1991 (Martin, 1990) based on an inverse
72 correlation between carbon dioxide and iron (inferred from aluminium data) in Vostok ice cores
73 linked with glacial and interglacial transitions. Martin proposed that increased Fe input to HNLC
74 oceanic regions as a result of higher dust loading could stimulate primary production. It was
75 further proposed that this effect could potentially cause intense drawdown of carbon dioxide,
76 reduce atmospheric temperatures and hence be an important driver of global climate change. A
77 recent study using a sediment core from the Subantarctic Atlantic Ocean has shown that during
78 glacial times an increase in dust flux resulted in higher productivity and nitrate consumption
79 which is consistent with Subantarctic iron fertilisation (Martinez-Garcia et al., 2014).

80
81 This iron limitation hypothesis has been tested in the under-productive waters of the Equatorial
82 Pacific (e.g. IronEx; Coale et al., 1996), Subarctic Northeast Pacific (Boyd et al., 2005) and
83 Southern Ocean (SOIREE; Boyd and Law, 2001) by seeding surface ocean waters with low
84 concentrations of dissolved iron. These *in situ* experiments triggered large phytoplankton
85 blooms that resulted in a significant drawdown of atmospheric carbon dioxide and surface water
86 nitrate. More recently it has been shown that iron also plays an important role in nutrient cycling
87 processes such as nitrogen fixation in the North and South Atlantic (Schlosser et al., 2014) and
88 can limit growth in non-HNLC regions and coastal upwelling areas (Bruland et al., 2001;
89 Capone and Hutchins, 2013; Chase et al., 2005). These observations highlight the need for
90 robust conceptual and numerical models of ocean biogeochemistry to include iron as a limiting
91 component (Moore and Doney, 2007; Tagliabue and Völker, 2011).

92
93 In order to provide accurate measurements of dissolved iron for the modelling community and to
94 understand the processes that control iron marine biogeochemistry, the species to be
95 determined must be clearly and operationally defined. Size fractionation is particularly important
96 due to the broad variety of Fe species thought to exist in seawater, including nanoparticles,
97 colloidal phases and macromolecules. Historically, dissolved iron has been defined as that
98 which passes through a 0.45, 0.4 or 0.2 μm filter membrane (Cutter et al., 2010; de Baar and de
99 Jong, 2001), but the development of trace metal clean ultra-filtration techniques (Gobler et al.,
100 2002; Nishioka et al., 2001; Wu et al., 2001) now allows improved characterisation of different
101 size fractions. For example, the total dissolved (dFe), (truly) soluble (sFe) and colloidal (cFe)
102 iron pools can be operationally defined by the pore size of the filtration membrane used, i.e. dFe
103 $<0.2 \mu\text{m}$; sFe $<0.02 \mu\text{m}$; cFe $0.02 - 0.2 \mu\text{m}$ (Ussher et al., 2010a), with the total dissolvable
104 (TDFe) iron pool being operationally defined as the fraction detected after acidification and long

105 term (> 6 months) storage without prior filtration (Ussher et al., 2013). A surface water profile of
106 sFe, dFe and TDFe in the Atlantic Ocean on the AMT 16 transect is shown in **Fig. 2**.

107
108 Iron usually has a nutrient-type vertical distribution in open ocean HNLC waters, with depleted
109 dFe concentrations of < 0.2 nM in surface waters (Boyd and Ellwood, 2010; de Baar and de
110 Jong, 2001), increasing to 0.4 – 0.7 nM below 500 m. Dissolved (defined as < 0.4 µm) iron
111 measurements from 354 samples at 30 stations in the North and South Pacific, Southern Ocean
112 and North Atlantic gave a mean dFe concentration of $0.76 \pm 0.25 \text{ nmol kg}^{-1}$ (n = 117) at depths
113 below 500 m with minimal inter-ocean variability (Johnson et al., 1997) in spite of variable
114 sources of iron and relatively short residence times in deep waters of ~ 70 – 200 yr. The
115 presence of strong iron binding organic ligands and/or equilibrium between dissolved and
116 suspended particulate iron were the most likely controlling factors. In the mixed layer, mean dFe
117 concentrations were $0.07 \pm 0.04 \text{ nmol kg}^{-1}$ (n = 112). More recently a study of > 13,000 global
118 measurements of dissolved iron found that in shelf waters the mean surface water dFe
119 concentration was $0.61 \pm 1.14 \text{ nM}$ (n = 382) and in deeper waters was $0.53 \pm 0.17 \text{ nM}$ (n = 20)
120 (Tagliabue et al., 2012). Open ocean (off-shelf) data showed a much clearer nutrient/scavenged
121 element profile, with a surface water dFe minimum of 0.31 ± 0.45 (n = 999) that increased with
122 depth to $0.54 \pm 0.26 \text{ nM}$ (n = 301) (Tagliabue et al., 2012). A summary of this dataset is shown
123 in **Fig. 3**. Dissolved iron residence times in the upper water column are very short, e.g. ~ 250
124 days in the Sargasso Sea (Jickells, 1999), due to biological uptake and physical mixing
125 processes (Hutchins et al., 1993).

126
127 The concentrations of the different physico-chemical species of iron in seawater are dependent
128 on the equilibrium between various particulate and dissolved phases (see **Fig. 4**), the rate of
129 each of the processes shown and the physical composition and condition of the seawater.
130 Under most natural conditions, iron is found in the +2 and +3 oxidation states and forms salts
131 with the majority of common anions. Redox transitions between the two oxidation states are
132 dependent on pH and electron activity (pE) (Morel and Hering, 1993). In aerated aqueous
133 solutions at circumneutral pH, the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ cation is hydrolysed to form polynuclear oxy-
134 hydroxides. A solubility of $\sim 10^{-11} \text{ M}$ has been reported for iron(III) hydroxide in 0.7 M NaCl (pH
135 8.1, 25 °C) where soluble iron was defined as the fraction which passed through a 0.02 µm filter
136 (Liu and Millero, 1999) and in seawater (Liu and Millero, 2002).

137
138 The solubility of Fe(II) greatly exceeds that of Fe(III). Under anoxic conditions, Fe(II) can be
139 found at mM concentrations but under oxic conditions at pH >5 it becomes unstable and

140 oxidizes rapidly. Hence oxic aqueous solutions at seawater pH are predicted to contain
141 negligible Fe(II) at equilibrium (Stumm and Morgan, 1996) although significant Fe(II)
142 concentrations can be found near sources such as hydrothermal plumes and in low oxygen
143 waters (Breitbarth et al., 2010). However, > 99 % of the dissolved iron pool is complexed by
144 organic iron-binding ligands (siderophores) (Gledhill and Buck, 2012) which means that iron
145 redox speciation in seawater is strongly linked with the concentrations and physico-chemical
146 properties of the iron complexes present. Two classes of strong iron binding ligands (L_1 and L_2)
147 have been characterised and determined in open ocean seawater, and their complexing ability
148 is expressed using conditional stability constants ($K_{Fe^{3+}L}$), i.e. $K_{Fe^{3+}L} = [FeL] / [Fe^{3+}] [L]$, where
149 $[Fe^{3+}]$ is the sum of the inorganic Fe(III) species (including hydroxide complexes). A range of
150 siderophores (generally low molecular mass hydroxamates, ferrioxamines and amphibactins) in
151 seawater have been identified using mass spectrometric techniques (Boiteau et al., 2013; Mawji
152 et al., 2008; Mawji et al., 2011; Velasquez et al., 2011).

154 2. Sampling and sample treatment

155 The quality of analytical data for iron concentrations in seawater is dependent on the acquisition
156 and storage of clean and stable samples and the availability of suitable detection methods. It is
157 therefore important that well documented protocols that reflect best practice are used for
158 sample collection and treatment in order to minimise contamination. Open discussion within the
159 community is also an essential part of this process. A good starting point for reliable sample
160 collection is the GEOTRACES 'cookbook' for micronutrient sampling and sample-handling
161 (Cutter et al., 2010). This has a specific section (section VI) dealing with sampling and handling
162 protocols for trace elements, including iron.

164 The first step is to ensure that trace metal-clean sampling apparatus and sample collection
165 bottles are used. For surface water sampling a clean surface pump sipper/tow fish system is
166 recommended (Cutter et al., 2010) such as the device reported by Vink *et al.* (Vink et al., 2000).
167 The key components of any surface sampling system are a clean pump (a PTFE diaphragm
168 pump is preferred but a peristaltic pump can also be used), clean plastic tubing on all lines and
169 a tow fish of suitable hydrodynamic design, material and density.

171 Several clean sampling systems have been reported for obtaining depth profiles. Since the
172 earliest reliable design of a discrete sampler for obtaining open ocean depth profiles (Bruland et
173 al., 1979) various devices and modifications have been reported (Bell et al., 2002; Cutter and
174 Bruland, 2012; de Baar et al., 2008; Fitzsimmons and Boyle, 2012; Measures et al., 2008;

175 Sedwick et al., 2005). Measures *et al.* described a commercially available rosette-based system
176 for trace metal-clean sampling (Measures et al., 2008) that was successfully deployed on
177 several CLIVAR cruises for high-resolution trace element sampling. De Baar *et al.* described a
178 fast and ultraclean system for sampling deep ocean waters for trace metals (de Baar et al.,
179 2008) constructed with a titanium frame and having 8000 m of Kevlar wire with internal power
180 and signal cables. Cutter and Bruland reported a system for the rapid and non-contaminating
181 sampling of trace elements with volumes of up to 36 L per depth for both dissolved and
182 particulate phases (Cutter and Bruland, 2012). Based on the use of this system on three major
183 cruises, the launch-sample-recover time for the carousel (2 bottles triggered per depth) was 1 h
184 per 1000 m, and dissolved and particulate sampling time averages were 6 h per hydrocast. In
185 all cases, the collected samples were then handled in a trace metal-clean laboratory on board
186 the ship, which should conform to ISO Class 5 specifications (ISO, 2010).

187
188 The next step in the process is sample storage, which requires the use of appropriate
189 containers and rigorous cleaning protocols for those containers. The GEOTRACES cookbook
190 (Cutter et al., 2010) recommends low density polyethylene (LDPE) or high density polyethylene
191 (HDPE) bottles for both the total dissolvable (unfiltered) and total dissolved (filtered) fractions for
192 most trace metal determinations, including iron. Rigorous sample bottle cleaning is essential
193 and in addition to the recommended protocol in the GEOTRACES guide there are several other
194 similar and effective strategies (e.g. Achterberg et al., 2001). For the determination of dissolved
195 iron ($< 0.2 \mu\text{m}$) it is necessary to filter the sample, for which a cartridge (capsule) type filter, with
196 $0.8/0.2 \mu\text{m}$ pore sizes, is recommended (Cutter et al., 2010). Polycarbonate membrane filters
197 have also been successfully used for smaller sample volumes (Bowie et al., 2010). To obtain
198 the soluble ($< 0.02 \mu\text{m}$) fraction an ultrafiltration membrane can be used (Schlosser et al.,
199 2013), usually in a cross flow configuration (Schlosser and Croot, 2008). Aluminium oxide
200 membranes have also been used (Wu et al., 2001).

201
202 For the determination of total dissolved iron, samples should be acidified using concentrated
203 hydrochloric acid to pH 1.7 - 1.8 (0.024 M) (Johnson et al., 2007). The acid should be as pure
204 as possible, with acidification blanks collected and analysed on a regular basis, and handling
205 must conform to the required standards of cleanliness. Acidification can be done at sea or when
206 samples are returned to the laboratory. For speciation analysis, e.g. the direct determination of
207 Fe(II), the analysis must be carried out immediately after sampling, and hence on-board ship,
208 because of its high reactivity. In this case two strategies are to buffer the sample to $\text{pH} \leq 7.2$ or
209 to cool it to $2 - 4 \text{ }^\circ\text{C}$ (Cutter et al., 2010).

210

211 3. Analytical methods

212 One of the earliest reported attempts to determine iron in seawater was in 1935 (Cooper, 1935).
213 A spectrophotometric method was used, with tripyridyl as the selective reagent; Fe(II),
214 “reducible” Fe (after treatment with HCl/sulphite) and “total” Fe (after treatment with
215 HCl/bromine water) were determined on 100 mL volumes of filtered seawater samples. Since
216 that time both laboratory and shipboard methods have evolved to a remarkable degree and
217 there are a number of relatively recent overviews of methods for the determination of dissolved
218 iron in seawater (Achterberg et al., 2001; Bowie and Lohan, 2009; Bruland and Rue, 2001).

219

220 The most common approach used to determine iron in seawater in the late 1970s and 1980s
221 was preconcentration using solvent extraction (Danielsson et al., 1985; Gordon et al., 1982;
222 Landing and Bruland, 1987; Spencer et al., 1970) or co-precipitation (Symes and Kester, 1985)
223 coupled with detection by electrothermal (graphite furnace) atomic absorption spectrometry
224 (ETAAS). Chelation with ammonium 1-pyrrolidinedithiocarbamate (APDC) and
225 diethylammonium diethyldithiocarbamate (DDDC), double extraction into chloroform and back-
226 extraction into nitric acid was the most popular solvent extraction approach (Bruland et al.,
227 1979). A detection limit of 50 pM was reported by Landing and Bruland (Landing and Bruland,
228 1987), with high reagent blanks and contamination during sample handling being the main
229 challenges at that time. On-line solid phase preconcentration became increasingly popular
230 during the 1980s and 1990s with Saager *et al.* reporting a detection limit of 150 pM using
231 Chelex-100 (Saager et al., 1989). In addition, these approaches typically required 250 mL - 4 L
232 of sample (Bruland et al., 1979).

233

234 In recent times, high resolution (magnetic sector) ICP-MS has become the preferred atomic
235 spectrometric method of detection, providing sensitive and time efficient iron determinations
236 whilst excluding isobaric interferences. Isotope dilution is often used for quantification, either
237 with co-precipitation or on-line solid phase preconcentration. An attraction of isotope dilution is
238 that it is an absolute and hence traceable method that does not require external standards or
239 standard additions. Hence matrix interferences and variations in recovery are not a significant
240 problem. Magnesium hydroxide co-precipitation (Wu, 2007; Wu and Boyle, 1998) requires
241 minimal use of reagents and hence gives a very low reagent blank, with reported detection
242 limits of 50 pM (Wu and Boyle, 1998) and 2 pM (Wu, 2007). On-line solid phase chelation has
243 reported detection limits of 15 pM with 8-hydroxyquinoline (8-HQ) immobilised on silica gel
244 (Akatsuka et al., 1992), 21 pM with Toyopearl AF-Chelate-650M (iminodiacetic acid chelating

245 group) (Milne et al., 2010), 70 pM with nitrilotriacetic acid (NTA) SuperflowTM resin (Lee et al.,
246 2011) and 14 pM with a “seaFAST” column (co-immobilised ethylenediaminetriacetic acid and
247 iminodiacetic acid chelating groups immobilised on a hydrophilic methacrylate polymer)
248 (Lagerstrom et al., 2013).

249
250 Quantitative recoveries can also be obtained using solid phase preconcentration and standard
251 additions to the seawater matrix without the need for isotope dilution, with reported detection
252 limits of 640 pM with 8-hydroxyquinoline immobilised on fluorinated metal alkoxide glass (Sohrin
253 et al., 1998) and 14 pM (Biller and Bruland, 2012) and 2000 pM (Sohrin et al., 2008), both with
254 the Nobias Chelate PA1 resin (co-immobilised ethylenediaminetriacetic acid and iminodiacetic
255 acid chelating groups). Millilitre sample volumes are required for ICP-MS, e.g. 12 mL was used
256 by Milne et al. with isotope dilution (Milne et al., 2010) and 40 mL by Biller and Bruland without
257 isotope dilution (Biller and Bruland, 2012). These data show the significant improvements that
258 have been made in recent years with regard to detection limits and sample volumes required for
259 the determination of dissolved iron in seawater, as well as the greater emphasis on method
260 validation using reference materials (see section 4 for further details).

261
262 ICP-MS and ETAAS can generate high quality data in a controlled laboratory environment but
263 there is a requirement for portable methods that can be used at sea, thereby providing rapid
264 analysis whilst minimising sample treatment and storage. In this context flow injection (FI)
265 techniques provide an excellent platform for sample handling (Zagatto et al., 2012). There are
266 two main detection systems used in conjunction with FI for the determination of dissolved iron,
267 namely chemiluminescence (CL) and spectrophotometry (SP) and typical manifold diagrams
268 are shown in **Fig. 5** (Bowie et al., 2004). With both systems preconcentration of iron onto a
269 chelating resin is a necessary requirement to concentrate the iron and separate it from the bulk
270 seawater matrix. The majority of FI techniques use 8-HQ as the functional chelating group
271 immobilised on a chemically-resistant vinyl polymer resin such as Toyopearl TSK (Landing *et*
272 *al.*, 1986). More recent studies have used commercially available chelating resins such as NTA
273 “Superflow” (Lohan et al., 2005) and Toyopearl AF-Chelate-650 (Hurst and Bruland, 2007),
274 thereby eliminating the synthesis step involved in using 8-HQ. Due to the speciation of iron, a
275 key consideration is the pH dependency on the recovery of Fe(III) and Fe(II) on the
276 preconcentration column. For example, Fe(III) is recovered by 8-HQ at pH 3.0 - 4.2, while at pH
277 5.2 - 6.0 both Fe(III) and Fe(II) are quantitatively recovered (Obata et al., 1993). Therefore, FI
278 may also allow the iron redox speciation measurements by careful selection of the pretreatment
279 pH, reagent conditions and an appreciation of possible interferences (Bowie et al., 2002;

280 Hopkinson and Barbeau, 2007; Ussher et al., 2005). For “total” dissolved iron (Fe(II) + Fe(III))
281 measurements, either an oxidation step (addition of 10 μ M hydrogen peroxide (Lohan et al.,
282 2006) or a reduction step (addition of 100 μ M sodium sulfite (Bowie et al., 1998) prior to
283 preconcentration is required.

284

285 FI-CL methods are based on the catalytic effect of either Fe(II) or Fe(III) ions on the oxidation of
286 luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) to generate blue luminescence (λ_{\max} ~440
287 nm) which is detected using a photomultiplier tube. FI-CL methods that determine Fe(II) require
288 acidified samples to be reduced off-line using, e.g., sodium sulphite (e.g. Bowie et al., 1998).
289 Reduced samples are then buffered in-line to pH 5 using ammonium acetate prior to
290 preconcentration on a suitable resin such as 8-HQ. Iron(II) ions are eluted from the resin using
291 HCl (e.g. 0.09 M) and merged with a luminol/carbonate buffer reagent stream. Bowie *et al.*
292 achieved a detection limit of 40 pM and 3.2 % RSD (n=5) for 1 nM iron (Bowie et al., 1998). FI-
293 CL methods that determine Fe(III) and total dissolved iron if acidified samples are first oxidised
294 off-line using hydrogen peroxide (Johnson et al., 2007; Klunder et al., 2011). Acidified, oxidised
295 samples are buffered in-line to pH 3 with ammonium acetate prior to preconcentration. Iron(III)
296 ions are eluted from the resin using HCl (e.g. 0.3 M). A 2 m heated coil is required to efficiently
297 mix the eluted Fe(III) with the luminol/carbonate buffer reagent and hydrogen peroxide streams
298 prior to detection. A mean blank for this method has been reported as 32 ± 14 pM Fe (n=19)
299 with a detection limit of 5.7 ± 2.9 pM Fe (n=4) (Klunder et al., 2011).

300

301 FI-SP involves the catalytic oxidation of DPD (N,N-dimethyl-p-phenylenediamine
302 dihydrochloride) by Fe(III) cycled with hydrogen peroxide (Lohan et al., 2006; Measures et al.,
303 1995). The catalysis increases the sensitivity of this method, as the amount of oxidised DPD is
304 proportional to the concentration of iron. Hydrogen peroxide (10 μ M) is added to the sample to
305 ensure complete oxidation of iron to Fe(III). In-line buffering of the sample is generally required
306 and is dependent on the resin used for preconcentration. Iron is eluted from the resin and mixes
307 with DPD/buffer and hydrogen peroxide, producing coloured semiquinone derivatives, which are
308 detected spectrophotometrically at 514 nm. The average blank for this method was 60 ± 8 pM
309 Fe (n=35) with a detection limit of 24 ± 4.9 pM Fe (n=9) (Lohan *et al.* 2006). SAFe surface
310 samples gave a mean \pm SD value of 0.10 ± 0.009 nM (n=14) and SAFe deep samples $0.93 \pm$
311 0.04 nM (n=18), in excellent agreement with the SAFe consensus values of 0.097 ± 0.007 nM
312 and 0.91 ± 0.17 nM respectively (Lohan et al., 2006).

313

314 Voltammetric techniques provide an alternative strategy for both the shipboard and laboratory
315 based determination of dissolved iron in seawater. The preferred variant of the technique is
316 cathodic stripping voltammetry (CSV) in which an iron-binding ligand is added to the seawater
317 sample to selectively form a complex with Fe(III). This complex is adsorbed onto the working
318 electrode, typically a hanging mercury drop, followed by cathodic stripping as the Fe(III) is
319 reduced. Detection limits are typically 80 – 100 pM (Croot and Johansson, 2000; Gledhill and
320 van den Berg, 1995). However, to determine total dissolved iron, the seawater sample needs to
321 be pre-treated to liberate iron from complexes with natural seawater ligands. The technique is
322 also used to determine the complexation capacity of Fe(III) with natural ligands using a
323 competitive ligand exchange approach (Buck et al., 2012; Croot and Johansson, 2000; Hassler
324 et al., 2013; Hawkes et al., 2013; Town and Van Leeuwen, 2005; Wu and Jin, 2009). The most
325 common ligands used for this purpose are 1-nitroso-2-naphthol (NN) (Gledhill and van den Berg,
326 1995), salicylaldoxime (SA) (Rue and Bruland, 1995), 2-(2-thiazolylazo)-p-cresol (TAC) (Croot
327 and Johansson, 2000) and dihydroxynaphthalene (DHN) (Obata and Van den Berg, 2001).

328

329 Measurements of the stable isotopes of dissolved iron in seawater may help to answer
330 important biogeochemical questions (e.g. Lacan et al., 2008). There are four naturally occurring
331 stable iron isotopes: ^{54}Fe (5.84%), ^{56}Fe (91.76%), ^{57}Fe (2.12%), and ^{58}Fe (0.28%), and isotopic
332 data are typically reported using a standard δ notation in units of per mil (‰) (deviations in parts
333 per 1000 relative to a reference ratio), using either $^{56}\text{Fe}/^{54}\text{Fe}$ or $^{57}\text{Fe}/^{54}\text{Fe}$ ratios (Johnson et al.,
334 2008). The investigation of natural mass-dependent isotopic fractionation of iron has been
335 boosted by the recent development of multiple-collector inductively coupled plasma mass
336 spectrometry (MC-ICP-MS; de Jong et al., 2007). Many natural marine processes fractionate
337 iron isotopes, suggesting great promise for seawater $\delta^{56}\text{Fe}$ as a new tracer of the pathways,
338 sources and sinks of iron in the ocean, and how iron is biologically cycled. The largest
339 fractionation of iron isotopes occur during redox changes (e.g., microbial Fe^{3+} reduction), as well
340 as differences in bonding, but these are expressed only in natural environments in which
341 significant quantities of iron are mobilised and separated. In addition, since iron concentrations
342 in seawater are very low (< 1 nM), there are significant challenges to separate and purify iron
343 from seawater without introducing contamination and to accurately determine $\delta^{56}\text{Fe}$ on the small
344 quantities of iron extracted (John and Adkins, 2010). Nonetheless, Conway et al. have
345 simultaneously determined Fe, Zn and Cd stable isotopes ($\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$) in seawater
346 using Nobias Chelate PA-1 chelating resin for extraction, followed by purification using anion
347 exchange chromatography and detection by double spike MC-ICP-MS (Conway et al., 2013a;
348 Conway et al., 2013b). The method was notable for the use of low sample volumes (only 1 litre)

349 and very low blanks compared with previously reported methods. In addition, iron isotopic data
350 have been used in palaeo-reconstructions of ancient anoxic and early oxygenated marine
351 environments (Rouxel et al., 2005).

352
353 *In situ* sensors, as distinct from shipboard techniques, are attractive because they are
354 potentially low cost, low maintenance and suitable for long term remote deployments. They can
355 also be interrogated remotely using wireless technologies and microwave transmitters (mobile
356 phones) (Angove et al., 2011). There are however challenges with regard to long term
357 stability/calibration, biofouling and sample conditioning, e.g. filtration. Ion-selective electrodes
358 can now be miniaturised and manufactured as disposable devices (Zuliani and Diamond, 2012)
359 and although they are suitable for monitoring freshwater systems they are often prone to matrix
360 interferences in seawater. Optical sensors can potentially overcome these issues and a
361 fluorescence quenching-based siderophore (parabactin) biosensor has been developed for the
362 direct measurement of Fe(III) in oceanic waters (Lam et al., 2006). The LOD was 40 pM, with a
363 reproducibility of 6% RSD (n = 10) for 1000 pM Fe(III) and a 50 – 1000 pM working range.

364
365 Roy *et al.* used changes in the infrared spectrum of the iron binding siderophore
366 desferrioxamine B covalently immobilised on a mesoporous silica film when complexed with
367 Fe(III) (Roy et al., 2008). The system had a detection limit of ~50 pM for a 1 L seawater sample
368 at pH 1.7 and was used to determine dissolved iron in the Subarctic Pacific. The device is
369 potentially deployable on autonomous research platforms for long term *in situ* monitoring.

370
371 *In situ* sensors have great potential for high resolution and low cost spatial and temporal
372 mapping of dissolved iron (and other species) in seawater, including the remote open-ocean,
373 but further development is still required, not least in sample presentation and treatment, in order
374 to ensure reliable, long term operation.

375 376 4. Quality assurance of iron data

377 Method validation has been defined as *“the confirmation by examination and the provision of*
378 *objective evidence that the particular requirements for a specific intended use are fulfilled”*
379 (ISO/IEC, 2005). In addition ISO/IEC 2005 states that *“the range and accuracy of the values*
380 *obtainable from validated methods (e.g. the uncertainty of the results, detection limit, selectivity*
381 *of the method, linearity, limit of repeatability and/or reproducibility, robustness against external*
382 *influences and/or cross-sensitivity against interference from the matrix of the sample/test object),*
383 *as assessed for the intended use, shall be relevant to the customer’s needs.”* It also proposes

384 five approaches to method validation that can be used individually or in combination: (i)
385 calibration using reference standards or reference materials, (ii) inter-laboratory comparisons,
386 (iii) comparison of results achieved with other methods, (iv) systematic assessment of the
387 factors influencing the results and (v) assessment of the uncertainty of the results based on
388 scientific understanding of the theoretical principles of the method and practical experience.

389
390 Early inter-laboratory comparisons for trace metals in seawater (Bewers et al., 1981; Landing et
391 al., 1995) reported inconsistent results with up to one order of magnitude degree of variability in
392 the quantification of the analytical blank and inaccuracies in system calibration. Two more
393 recent intercomparison exercises that focussed on the determination of iron (both on board ship
394 and in the laboratory) were IRONAGES, using Atlantic Ocean samples collected in 2000 (Bowie
395 et al., 2003; Bowie et al., 2006), and SAFe (Sampling and Analysis of Fe), using Central North
396 Pacific samples collected in 2004 (Johnson et al., 2006; Johnson et al., 2007). A summary of
397 the analytical methods used by participating laboratories in the IRONAGES intercomparison
398 exercise is shown in **Table 1**. Both of these exercises also produced “in-house” seawater
399 reference materials with “consensus values” for the concentration of dissolved iron. These were
400 made available to the marine biogeochemistry community in response to the unavailability of
401 commercial seawater certified reference materials (CRMs) with suitably low certified
402 concentrations for iron. As an example of the use of these reference materials, Ussher *et al.*
403 compared the results obtained for the IRONAGES sample by FI-CL with isotope dilution ICP-
404 MS and found good agreement over a concentration range of 0.15 - 2.1 nM iron (Ussher et al.,
405 2010b) and any differences were attributed to random effects such as variable contamination
406 rather than systematic effects.

407
408 The marine biogeochemistry community has now established GEOTRACES
409 (<http://www.geotraces.org/>) to facilitate the study of the global marine biogeochemical cycles of
410 a suite of trace elements and their isotopes (TEIs), including iron (SCOR Working Group, 2007).
411 GEOTRACES conducted two intercalibration cruises, one in the North Atlantic Ocean at the
412 BATS (Bermuda Atlantic Time Series) site in 2008 and one at the SAFe site in the oligotrophic
413 North Pacific in 2009, and collected seawater for the preparation of ‘in-house’ reference
414 samples at both sites. A summary of the analytical methods used by participating laboratories
415 during analysis of the North Atlantic GEOTRACES reference sample to determine a consensus
416 value for dissolved iron in the North Atlantic is shown in **Table 2**. The ultimate goal for the
417 intercalibration component of GEOTRACES (Cutter, 2013) is to achieve the best possible
418 accuracy (lowest random and systematic errors) for these TEIs by evaluating and developing

419 GEOTRACES sample acquisition, handling, and storage protocols (Cutter et al., 2010),
420 identifying existing GEOTRACES primary standards and certified reference materials (CRMs)
421 and, where needed, producing suitable reference materials (RMs) or primary standards.

422

423 In the last few years there has been a proliferation of both new methods and new laboratories
424 reporting dissolved iron concentrations in seawater and rigorous quality assurance is therefore
425 essential. The most common methods use commercially available chelating resins such as
426 Nobias Chelate PA1 (e.g. Sohrin et al., 2008) and ICP-MS detection (e.g. Biller and Bruland,
427 2012; Lagerstrom et al., 2013; Milne et al., 2010). There are also commercially available
428 preconcentration systems such as “seaFAST” that automate the sample handling steps
429 (Hathorne et al., 2012; Lagerstrom et al., 2013), which should also improve precision. During
430 the IRONAGES intercomparison exercise seven different analytical techniques were used
431 (Bowie et al., 2006) whereas eighteen different methods have been used to date in the
432 GEOTRACES programme to produce consensus values for dissolved iron in surface (GS) and
433 deep (GD) seawater RMs

434 <http://es.ucsc.edu/~kbruland/GeotracesSaFe/kwbGeotracesSaFe.html>. These RMs are
435 available free of charge and allow laboratories to assess the accuracy and precision of their
436 measurements and also facilitate the development of new analytical methods.

437

438 All of these intercalibration efforts have greatly improved the accuracy of dissolved iron
439 measurements in seawater. This has enabled international programmes such as CLIVAR and
440 GEOTRACES that engage in ocean basin scale mapping of dissolved iron concentrations to
441 ensure that temporally and spatially variable data from different cruises, obtained by different
442 researchers using different analytical methods, can be reliably intercompared. A key aspect of
443 the sampling strategy is the use of cross-over stations whereby two or more cruises carrying out
444 ocean scale mapping have at least one common station where they determine the
445 concentration of dissolved iron, often using different sampling systems and, in some cases,
446 different analytical techniques. Both sample concentrations and RM consensus values are
447 compared to ensure that acceptable intercalibration is achieved. Deep water values are
448 preferred because surface waters values are impacted by seasonal changes in productivity and
449 inputs from atmospheric sources. The GEOTRACES programme has recently released an
450 intermediate data product and an atlas of dissolved Fe measurements in seawater
451 (<http://www.egeotraces.org/>) which is enabling a paradigm shift in our understanding of iron
452 cycling in seawater. An example of the data product showing a screen shot of an animated 3D
453 scene of reported dFe concentrations in the Atlantic Ocean is given in **Fig. 6**.

454

455 Uncertainty is one aspect of method validation and can be defined as the ‘parameter,
456 associated with the result of a measurement that characterises the dispersion of the values that
457 could reasonably be attributed to the measurand’ (JCGM, 2012). A simple statistical procedure
458 is often used by chemical oceanographers to estimate the uncertainty of a measurement result,
459 e.g. the internal instrumental precision obtained for analysis of a single sample is calculated to
460 give the range within which the stated result is likely to lie. However, this may underestimate the
461 uncertainty of a measurement, leading to over-interpretation of the significance of the result.
462 Evaluation of uncertainty is more reliably done using a mathematical model coupled with some
463 numerical method of differentiation that combines the individual uncertainties associated with
464 each model parameter, i.e. each of the steps in the sample collection, pre-treatment, storage
465 and measurement processes (Worsfold et al., 2013). Prior knowledge of the major sources of
466 input to the measurement results, and their associated uncertainties, will indicate where to focus
467 efforts to meet the target uncertainty. Further details of the approach can be found in “The
468 Guide for Uncertainty in Measurements”, often abbreviated to “the GUM”, (JCGM, 2008) and,
469 more specifically, in the Eurachem/CITAC Guide “Quantifying Uncertainty in Analytical
470 Measurement” (Ellison and Williams, 2012).

471

472 5. Future perspectives

473 With regard to sampling, there are developments in autonomous samplers, gliders, buoys and
474 Argo floats that offer great potential for the acquisition of long term time series samples, higher
475 sampling frequency, greater spatial coverage and regular access to more remote locations.
476 More use could also be made of ships (and submarines) of opportunity. However deployment of
477 these devices needs to be accompanied by improved sample treatment at the point of collection
478 and/or coupling with *in situ* measurement technologies. At present, laboratories are collecting
479 samples at a faster rate than their capacity to analyse them.

480

481 There is also a need for new measurement technologies, with the emphasis on fast, selective
482 methods with good accuracy and precision that need minimal sample treatment or can be used
483 directly, i.e. *in situ* sensors. This requires greater collaboration between the Analytical
484 Chemistry and Chemical Oceanography communities, supported by meetings such as that
485 hosted in Hawaii in 2013 (COCA Working Group, 2013). It also requires community wide
486 protocols for assessing and reporting data and for estimating uncertainty.

487

488 From a biogeochemistry perspective the same rigorous approach to sampling, analysis and
489 data treatment needs to be applied to the determination of particulate iron (Cutter et al., 2010)
490 and aerosol derived iron (Morton et al., 2013) and the GEOTRACES community is at present
491 focussing on the intercalibration of these two important measurements. Methods for the
492 determination of iron speciation also need to be critically evaluated and stable reference
493 materials for speciation studies developed.

494

495 Acknowledgements

496 The authors thank Dr. Robert Clough for helpful discussions on the Quality Assurance section.
497 Dr Clough is funded by the EMRP *via* JRP-ENV05-REG1 (Metrology for ocean salinity and
498 acidity). The EMRP is jointly funded by the EMRP participating countries within EURAMET and
499 the European Union. PW acknowledges funding from the Marine Institute, Plymouth University.
500 SU acknowledges funding from the European Commission via a Marie Curie Career Integration
501 Grant (PCIG-GA-2012-333143 DISCOSAT). ML acknowledges funding from the Natural
502 Environment Research Council (NERC) grant NE/H0004475/1). ARB acknowledges funding
503 from the Australian Research Council (FT130100037) and the Antarctic Climate and
504 Ecosystems Cooperative Research Centre.

505

Table 1. Analytical methods used during the IRONAGES iron intercomparison (Bowie et al., 2006).

Acronym	Summary	Reference(s)
CSV-DHN	Competitive ligand equilibration - cathodic stripping voltammetry (ligand: 2,3-dihydroxynaphthalene)	(Obata and Van den Berg, 2001)
FI-CL Fe(II)	Flow injection – luminol chemiluminescence (using dissolved O ₂ , sulfite reduction to FeII); preconcentration on 8HQ resin	(Bowie et al., 1998; King et al., 1995)
FI-CL Fe(III)	Flow injection - luminol chemiluminescence (using H ₂ O ₂ , natural oxidation to FeIII); preconcentration on 8HQ resin	(de Jong et al., 1998; Obata et al., 1993)
FI-SP	Flow injection - catalytic spectrophotometry (reagent: <i>N,N</i> -dimethyl- <i>p</i> -phenylenediamine dihydrochloride); preconcentration on 8HQ resin	(Measures et al., 1995)
ID-ICP-MS	Mg(OH) ₂ co-precipitation, isotope dilution - inductively coupled plasma mass spectrometry	(Wu and Boyle, 1998)
SE-ETAAS	Chelation solvent extraction - electrothermal atomic absorption spectrometry (ligand: APDC/DDDC)	(Bruland et al., 1979)
SPE-ICP-MS	Solid phase extraction - inductively coupled plasma mass spectrometry (ligand: bis(2-hydroxyethyl) dithiocarbamate, C ₁₈ column)	(Fujishima et al., 2001; Wells and Bruland, 1998)

Table 2. Analytical methods used during the analysis of the North Atlantic GEOTRACES reference sample to determine a consensus value for dissolved iron (adapted from http://es.ucsc.edu/~kbruland/GeotracesSaFe/2012GeotracesSAFeValues/GEOTRACES_Ref_Fe.pdf).

Acronym	Summary	Reference(s)
ID-ICP-MS	Concentrated off-line with the Mg(OH) ₂ co-precipitation method and analysed by isotope dilution ICP-MS. Blanks were quantified using 50 µL of sample instead of 1.6 mL. A single co-precipitation step was carried out followed by dilution of the precipitate with 4% HNO ₃ .	(Wu and Boyle, 2002)
ID-ICP-MS	Double co-precipitation with Mg(OH) ₂ and isotope dilution ICP-MS.	(Wu, 2007)
FI-SP	Flow injection using the NTA-type resin and DPD catalytic enhancement of the UV-visible absorption signal.	(Lohan et al., 2006)
SPE-ICP-MS	Off line concentration using an EDTriA-type chelating resin with subsequent analyses by ICP-MS.	(Sohrin et al., 2008)
SE-ICP-MS	Concentrated by solvent extraction and analysed by ICP-MS. 100 g seawater samples were buffered to a pH of 4.5 with purified ammonium acetate buffer. Purified ammonium pyrrolidinedithiocarbamate (PDC) and sodium diethyldithiocarbamate (DDC) were added to the samples which were then extracted twice by shaking following the addition of purified chloroform. The two chloroform extracts obtained were combined, acidified with nitric acid, shaken for 1 min and then diluted with purified water.	(Bruland et al., 1979)
SE-ETAAS	300–500 g portions of the samples were subjected to a dithiocarbamate–freon	(Danielsson et

	extraction modified from the procedure by implying maximum concentration factors of al., 1978; 500. The final extracts with the metals were measured by electrothermal atomic absorption spectrometry with Zeeman background correction (ETAAS; Perkin-Elmer Model 4100 ZL).	Kremling and Streu, 2001)
SPE-ICP-MS	Off-line concentrations using an EDTri-A-type chelating resin with subsequent analyses by ICP-MS. The method entailed an eight column manifold enabling eight separate 40 mL samples.	(Biller and Bruland, 2012; Sohrin et al., 2008)
ID-ICP-MS	Off-line extraction using IDA Toyopearl AF-Chelate-650 M resin followed by analysis using isotope dilution ICP-MS Prior to extraction the samples (12 mL) were buffered to pH ~6.2.	(Milne et al., 2010)
SPE-ICP-MS	On-line flow injection analysis of 4 mL of sea water using an EDTA-type chelating resin at pH 6 utilising purified ammonium acetate buffer and eluting analytes with 1.5 M HNO ₃ followed by detection with ICP-MS.	(Sohrin et al., 2008)
FI-CL	Flow Injection with chemiluminescence detection.	
ID-ICP-MS	100-bead NTA resin separation on small samples together with isotope dilution and ICP-MS detection.	(Lee et al., 2011)
FI-CL	Flow injection analysis with chemiluminescence detection.	(Sedwick et al., 2008)
FI-CL Fe(II)	Flow injection analysis with the Fe(II) luminol chemiluminescence method using sulfite reduction and NTA resin preconcentration.	(King and Barbeau, 2007)
CSV	Adsorptive cathodic stripping voltammetry of UV oxidised samples.	(Rue and

ETAAS	The final extracts were measured by electrothermal atomic absorption spectrometry.	Bruland, 1995) (Kremling and Streu, 2001)
FI-CL	Flow Injection with chemiluminescence detection using IDA Toyoparl AF-Chelate-650 M resin.	(Klunder et al., 2011)
ID-ICP-MS	Off-line batch preconcentration of 50 mL of acidified sample with NTA-type resin and analysed by isotope dilution MC-ICP-MS on a Nu Plasma instrument. Iron was analysed in low-resolution mode with a desolvating sample introduction system (Cetac Aridus 2). Concentrations calculated using the ratios between ^{57}Fe or ^{56}Fe and the added ^{54}Fe spike were internally consistent.	(de Jong et al., 2008)
ID-ICP-MS	On-line flow injection with a modified seaFAST system, the Nobias PA-1 resin, isotope dilution and ICP-MS detection.	
ID-ICP-MS	Off-line extraction with Nobias PA-1 chelating resin and analysis on an Element XR ICP-MS.	
SPE-ICP-MS	Off-line extraction using a WAKO chelating resin followed by analysis on an Element XR ICP-MS. Samples were UV digested for 3 h.	(Kagaya et al., 2009)
ID-ICP-MS	NTA resin bead preconcentration and MC-ICP-MS detection.	(Lee et al., 2011)

Figure captions

Figure 1

Approximations for annual global fluxes of dissolved iron (dFe) to the surface ocean (values are reported in or calculated from Bowers and Yeats, 1977; Chester and Jickells, 2012; Stallard and Edmond, 1983; Tagliabue et al., 2014). Riverine flux is estimated on the basis of 90% loss from estuarine mixing (Boyle et al., 1977). The sinking particulate flux (including scavenging) assumes a steady state and no other significant sinks.

Figure 2

Surface water iron size speciation profiles for the Atlantic Ocean on the Atlantic Meridional Transect (for AMT16), 20th May – 28th June 2005 showing soluble iron (sFe, <0.02 μm), dissolved iron (dFe, <0.2 μm), and total dissolvable iron (TDFe, unfiltered seawater). Reproduced with the permission of the authors from “Impact of atmospheric deposition on the contrasting iron biogeochemistry of the North and South Atlantic Ocean”, S. J. Ussher et al., *Global Biogeochemical Cycles*, 27 (2013) 1, doi: 10.1002/gbc.20056 (Ussher et al., 2013). The inset shows the cruise track for AMT16.

Figure 3

Box and whisker plots of dFe by (a) region and (b) basin. The size of the box represents the 1st to 3rd quartiles, with the vertical bar corresponding to the median and the whiskers representing 1.5 times the inter-quartile range. Reproduced with the permission of the authors from “A global compilation of dissolved iron measurements: Focus on distributions and processes in the Southern Ocean”, Tagliabue et al., *Biogeosciences*, 9 (2012), doi: 2333 10.1029/2003GL017721 (Tagliabue et al., 2012).

Figure 4

Phase transfers of iron and related processes in seawater. This figure was originally published by CSIRO Publishing in *Environmental Chemistry* 1, 67-80. doi: 10.1071/EN04053 <http://www.publish.csiro.au/paper/EN04053.htm> and is reproduced with their permission (Ussher et al., 2004).

Figure 5

Two flow injection manifolds for the determination of dissolved iron in seawater: (A) with chemiluminescence detection (FI-CL), and (B) with spectrophotometric detection (FI-SP).

Reproduced with permission from A.R. Bowie, P.N. Sedwick and P.J. Worsfold, *Limnology and Oceanography: Methods* (Association for the Sciences of Limnology & Oceanography), 2004, 2, “Analytical intercomparison between flow injection – chemiluminescence and flow injection-spectrophotometry for the determination of picomolar concentrations of iron in seawater”, p 45. Copyright 2014 by the Association for the Sciences of Limnology and Oceanography, Inc. (Bowie et al., 2004).

Figure 6

Screen shot of the GEOTRACES animated 3D scene of reported dFe concentrations in the Atlantic Ocean. Reproduced with permission from Schlitzer, R., *eGEOTRACES - Electronic Atlas of GEOTRACES Sections and Animated 3D Scenes*, <http://www.egeotraces.org>, 2014. Original data supplied by Andrew Bowie, Ken Bruland, Tim Conway, Hein de Baar, Fanny Chever, Seth John, Maarten Klunder, Patrik Laan, Francois Lacan, Rob Middag, Abigail Noble, Micha Rijkenberg, Mak Saito, Geraldine Sarthou, Peter Sedwick and Jingfeng Wu (Schlitzer, 2014).

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