

Dissolved Iron – all values in nM – labs are anonymous

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A	0.091 ± 0.005	0.910 ± 0.032	0.100 ± 0.012	0.054
Lab B	0.089 ± 0.016	0.92 ± 0.07		
Lab C	0.090 ± 0.002	0.916 ± 0.005	0.048 ± 0.009	0.027
Lab D	0.084 ± 0.003		0.016 ± 0.001	0.002
Lab E	0.094 ± 0.008	0.918 ± 0.027	0.096 ± 0.006	0.018
Lab F	0.09 ± 0.02	0.92 ± 0.05		
Lab G	0.092 ± 0.005	0.934 ± 0.035		
Lab H	0.088 ± 0.006	0.906 ± 0.048		
Lab I	0.107	0.874	0.048 ± 0.006	0.018
Lab J	0.095 ± 0.015	0.884 ± 0.036	0.32 ± 0.003	0.010
Lab K	0.084 ± 0.017	0.93 ± 0.10		
Lab L	0.095 ± 0.031	0.942 ± 0.062	0.023 ± 0.011	0.033
Lab M	0.089 ± 0.021	0.939 ± 0.047	0.059 ± 0.017	0.051
Lab N		0.99 ± 0.05		
Lab O	0.100 ± 0.015	0.915 ± 0.027	0.013 ± 0.010	0.020
Lab P	0.107 ± 0.002	0.90 ± 0.01	< 0.01	0.03
Lab Q	0.11 ± 0.01	0.97 ± 0.06		0.03

Lab R	0.111 ± 0.005		0.269 ± 0.014	0.043
Lab S	non detected	0.72 ± 0.19	0.02 ± 0.01	0.03

SAFe S = 0.094 ± 0.008 nM

SAFe D2 = 0.923 ± 0.029 nM

SAFe D1 ~ 0.65 ± 0.10 (with lower D1 bottle #'s being slightly higher and high D1 bottle #'s being slightly lower – ranging from 0.70 to 0.55 nM).

The above concentrations are consensus values for the SAFe reference samples (± 1 standard deviation). Data from Labs R and S were not used.

There was no significant difference between samples pretreated with a UV oxidation step and those without the UV treatment.

These consensus values on the SAFe reference samples for dissolved Fe are similar to those determined on board ship and reported by Johnson et al. (2007).

Less data is available (not shown) for SAFe D1.

References:

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Labs participating in the analysis of the SAFe reference samples to determine consensus values for dissolved Fe (listed in random order):

Mike Gordon/Kenneth Coale (MLML, U.S.) :

Dissolved Fe was concentrated by solvent extraction with PDC/DDC (Bruland et al., 1979) and subsequently analyzed by ICP-MS.

Geoff Smith/Ken Bruland (UCSC, U.S.):

Dissolved Fe was concentrated by solvent extraction with PDC/DDC (Bruland et al. 1979) and subsequently analyzed by graphite furnace atomic absorption spectrometry (GFAAS).

Ana Aguilar-Islas/Jingfeng Wu (UAF, U.S.):

Concentrated off-line with the $Mg(OH)_2$ coprecipitation method (Wu and Boyle, 1997) and analyzed by isotope dilution ICP-MS. Iron was analyzed in mid resolution mode, using the ratio between the natural abundance of ^{56}Fe and an added ^{57}Fe spike. 1.6ml of sample and spike were allowed to equilibrate for several minutes. A single co-precipitation step was carried out followed by dilution of the precipitate with 4% HNO_3 .

Jingfeng Wu (UAF, U.S.):

A double co-precipitation with $Mg(OH)_2$ and isotope dilution ICP-MS.

Maevae Lohan (Plymouth Univ., U.K.):

Flow injection using the NTA-type resin and DPD catalytic enhancement of the UV-Vis absorption signal (Lohan et al., 2006).

Yoshiki Sohrin (U. Kyoto, Japan):

Off line concentration using an EDTA-type chelating resin with subsequent analyses by ICP-MS using the method of Sohrin et al. (2008).

Michael Ellwood (Australian National U, Australia):

Dissolved Fe was concentrated by solvent extraction (Bruland et al., 1979) and analyzed by ICPMS. 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.

Peter Croot/Peter Streu (IMF/GEOMAR, Germany):

Samples were analyzed according to the method described in Kremling and Streu (2001). For the analysis of Cd, Co, Cu, Fe, Ni, Pb and Zn, 300–500 g portions of the samples were subjected to a dithiocarbamate–freon extraction modified from the procedure by Danielsson et al. (1978) implying maximum concentration factors of 500. The final extracts with the metals were measured by electrothermal atomic absorption spectrometry with Zeeman background correction (ETAAS; Perkin-Elmer Model 4100 ZL).

Dondra Biller/Ken Bruland (UCSC, U.S.):

Off-line concentrations using an EDTA-type chelating resin with subsequent analyses by ICP-MS based upon the method of Sohrin et al. (2008). The method entailed a six column enabling six separate 75 mL samples that had been UV oxidized, then adjusted to pH 6.5 with ammonium acetate, and simultaneously concentrated on the six resin columns. The resin columns were rinsed and then eluted with 3 mL of 1 N nitric acid for a concentration factor of ~25.

Angie Milne/Bill Landing (FSU, U.S.):

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.

Matt Hurst (HSU, U.S.):

On-line flow injection using IDA Toyopearl AF-Chelate resin with analyses by ICP-MS (Hurst and Bruland, 2008).

Geoff Smith/Ken Bruland (UCSC, U.S.):

On-line flow injection analysis of 4 ml of sea water using an EDTA-type chelating resin (Sohrin et al., 2008) at pH 6 utilizing purified ammonium acetate buffer and eluting analytes with 1.5 M HNO₃ followed by detection with ICP-MS

Bill Hiscock/Chris Measures (UH, U.S.):

Use of 8-hydroxyquinoline chelating resin off-line with subsequent analysis by isotope dilution ICP-MS.

Ed Boyle (MIT, U.S.):

100-bead NTA resin separation on small samples together with isotope dilution and ICP-MS detection.

Pete Sedwick (ODU, U.S.)

Flow injection analyses with chemiluminescence detection (Sedwick et al., 2008).

Kathy Barbeau (SIO/UCSD, U.S.):

Flow injection analysis with the Fe(II) luminol chemiluminescence method using sulfite reduction and NTA resin preconcentration, as described in King and Barbeau (2007).

Kristen Buck (BIOS, Bermuda):

Adsorptive cathodic stripping voltammetry of UV oxidized samples using the method of Rue and Bruland (1995).

Jeff Mendez (CIT, U.S.):

Mg(OH)₂ coprecipitation with ICP-MS (Mendez et al., 2008).

Patrick Laan/Maarten Klunder/Hein de Baar (NIOZ, Netherlands)

Flow Injection with chemiluminescent detection (Klunder et al., submitted) using IDA Toyopearl AF-Chelate-650 M resin.

Veronique Schoemann/Jeroen de Jong (U. Libre de Bruxelles, Belgium):

Off-line batch preconcentration of 50 mL of acidified sample with NTA-type resin and analyzed by isotope dilution MC-ICP-MS on a Nu Plasma instrument (de Jong et al. 2008). Iron was analyzed in low-resolution mode with a desolvating sample introduction system (Cetac Aridus 2).

Concentrations calculated using the ratios between ⁵⁷Fe or ⁵⁶Fe and the added ⁵⁴Fe spike were internally consistent.

The figure below presents published and unpublished data from the SAFe station in fall 2004 (Maeve Lohan's dissolved Fe data on samples from the CLIVAR rosette system in the upper 1000 meters (Lohan et al. 2006), and Jingfeng Wu's data from samples collected with the CLIVAR sampler) compared with historical data of John Martin from a nearby VERTEX station (Martin and Gordon, 1988). The consensus values for the SAFe reference samples are shown. The SAFe D1 sample was aliquoted from an unacidified tank with nitrogen gas pressure used to disperse the samples. During this time carbon dioxide degassed, the pH increased, and some dissolved Fe was lost to the walls of the SAFe tanks. The tanks were rinsed and filled again, and this time the tank was acidified prior to aliquoting the 0.5 L reference samples for the SAFe D2 samples.

