

Dissolved Cobalt – all values in pM – labs are anonymous

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A - non UV	2.6 ± 0.5	25.1 ± 1.0	4.4 ± 0.16	0.5
Lab B - non UV	2.7 ± 0.7	22.0 ± 1.0		
Lab C - non UV	< 5	23.8 ± 2.9		
w/ UV	< 7	41.2 ± 0.3	4.2 ± 1.5	5
Lab D - non UV	3.8 ± 0.2	30.4 ± 1.5	< 2	2
Lab E - non UV	3.9 ± 0.8	31.2 ± 2.0	1.5 ± 0.3	0.9
Lab F – w/ UV	4.9 ± 1.2	43.4 ± 1.2	0.09 ± 0.04	0.13
Lab G - w/ UV	3.9 ± 1.0	40.6 ± 3.6	2.5 ± 0.6	1.8
non UV		30.1 ± 3.7		
Lab H - non UV	1 ± 1	23 ± 1	7.0 ± 0.4	1.2
w/ UV	3 ± 2	44 ± 3		
Lab I - w/ UV	2.2 ± 1.5	40.5 ± 1.7	5.7 ± 1.1	3.2
Lab J - non UV	1 ± 1	25 ± 3		
w/ UV	7 ± 1.4	49 ± 6		
Lab L – non UV	< 10	22.6	6 ± 2	5
Lab M - non UV	4 ± 1	36 ± 10		

Consensus values on samples that were UV-oxidized prior to analysis:

SAFe S = 4.2 ± 1.9 pM

SAFe D2 = 43.1 ± 3.2 pM

The above average values (and ± 1 standard deviation) were determined using data from samples that were pretreated with a UV oxidation step.

It is clear that a UV oxidation step (or the development of a new chemical treatment) is necessary to determine the total dissolved Co in the SAFe reference samples. Even with UV pre-treatment, there is still too much variation in the values. More research needs to be performed evaluating the intensity and duration of the UV pre-treatment required to release all the cobalt for the various analytical methods. The eventual consensus values may turn out to be higher than the above current estimates.

In contrast, the values listed below are the averages of the various labs for samples that were not pretreated with a UV oxidation step.

SAFe S = 2.7 ± 1.3 pM

SAFe D2 = 26.9 ± 4.7 pM

There is much less data available for the SAFe D1 sample (not shown), and it appears similar to the D2 sample.

References:

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3. Cannizzaro, V., A.R. Bowie, A. Sax, E.P. Achterberg and P.J. Worsfold. Determination of cobalt and iron in estuarine and coastal waters using flow injection with chemiluminescence detection. *Analyst*, **125**: 51-57 (2000).
4. Hurst, M.P. and K.W. Bruland. The effects of the San Francisco Bay plume on trace metal and nutrient distributions in the Gulf of the Farallones. *Geochimica et Cosmochimica Acta*, **72**: 395-411 (2008).
5. Kremling, K. and P. Streu. Behaviour of dissolved Cd, Co, Zn, and Pb in North Atlantic near-surface waters (30°N/60°W to 60°N/2°W). *Deep Sea Research I*, **48**(12): 2541-2567 (2001).
6. Saito, M.A. and J.W. Moffett. Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. *Marine Chemistry*, **75**:49-68 (2001).
7. Sohrin, Y., S. Urushihara, S. Nakatsuka, T. Kono, E. Higo, T. Minami, K. Norisuye, and S. Umetani. Multielemental determination of GEOTRACES key trace metals in seawater by ICP-MS after preconcentration using an ethylenediaminetriacetic acid chelating resin. *Analytical Chemistry*, **80**: 6267-6273 (2008).
8. Wu., J. and E.A. Boyle. Low blank preconcentration technique for the determination of lead, copper and cadmium in small volume seawater samples by isotope dilution ICP-MS. *Analytical Chemistry*, **69**: 2465-2470 (1997).

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

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

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

Jingfeng Wu (UAF, U.S.):

Concentrated off-line with the Mg(OH)₂ coprecipitation method (Wu and Boyle, 1997) and analyzed by ICP-MS.

Rachel Shelley/Maeve Lohan (U. Plymouth, U.K.):

Flow injection chemiluminescence method modified after Cannizzaro et al. (2000). Modifications included UV-oxidation, use of IDA Toyopearl AF Chelate resin and an ammonium acetate conditioning and rinse step.

Abigail Noble/Mak Saito (WHOI, U.S.):

Adsorptive cathodic stripping voltammetry based upon modifications of Saito and Moffett (2000).

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).

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

Off-line concentration using an EDTA-type chelating resin with subsequent analyses by ICP-MS based upon the method of Sohrin et al. (2008). The method entails a six column manifold enabling six separate ~ 75 mL samples to be processed simultaneously. The samples were UV oxidized for 1.5 hrs, amended with H₂O₂ (final concentration of 10 µM), and adjusted to pH 6.5 with ammonium acetate prior to the concentration step. The resin columns were rinsed with a weak ammonium acetate buffer at a pH of 6.5 and eluted with 3 mL of 1 N nitric acid for a concentration factor of ~25, with subsequent analyses by ICP-MS. The Mo interference and correction were greatly reduced with the use of a PC3-SSI Peltier, water-cooled, spray chamber (Elemental Scientific Inc.).

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).

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

Off-line extraction using IDA Toyopearl AF-Chelate resin followed by analysis using ICPMS. Prior to extraction the samples (12 mL) were UV oxidized and buffered to pH ~6.2.

Michael Ellwood (Australian National U, Australia):

Concentrated by solvent extraction (Bruland et al., 1979) and analyzed 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. Trace metal concentrations were determined by ICP-MS (820-MS Varian, Australia).

Pete Morton/John Donat/Bill Landing (ODU/FSU, U.S.):

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

Matt Hurst (HSU, U.S.):

On-line flow injection using IDA Toyopearl AF-Chelate resin with analyses by ICPMS (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 1.5M HNO₃ followed by detection with ICPMS.

The figure below presents the UV treated and non-UV treated SAFe data compared with historical data from a nearby station (Martin and Gordon, 1988). The consensus value for the non-UV treated SAFe D2 reference sample is similar to values reported by Martin and Gordon, however the UV treated SAFe D2 consensus value is higher.

