

## Dissolved Copper – all values in nM – labs are anonymous

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A - non UV w/ isotope dilution	0.52 ± 0.05	2.33 ± 0.09	0.10 ± 0.03	0.10
Lab B - non UV w/ isotope dilution	0.58 ± 0.05	2.49 ± 0.10	0.06 ± 0.04	0.12
Lab C - non UV	0.36 ± 0.06	1.92 ± 0.06	< 0.01	0.01
Lab D - non UV	0.50 ± 0.02	1.95 ± 0.13	0.008 ± 0.002	0.007
Lab E - non UV	0.51 ± 0.05	2.15 ± 0.09		
Lab F - w/ UV	0.58 ± 0.09	2.26 ± 0.35	0.044 ± 0.005	0.015
Lab G - non UV	0.49 ± 0.04	2.28 ± 0.03	0.043 ± 0.001	0.003
w/ UV	0.61 ± 0.07	2.58 ± 0.08		
Lab H - w/ UV	0.53 ± 0.02	2.10 ± 0.13	0.02 ± 0.01	0.03
Lab I - non UV	0.44 ± 0.01	1.84 ± 0.06	0.02 ± 0.02	0.05
Lab J - w/ UV	0.51 ± 0.01			
Lab J - w/ UV	0.51 ± 0.01		< 0.01	0.03
Lab K – non UV	0.51 ± 0.01	2.01 ± 0.14	0.075 ± 0.005	0.01
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Lab L - non UV w/ isotope dilution	0.58 ± 0.01	2.77 ± 0.07		
Lab M - non UV	0.396	1.69	0.004 ± 0.001	0.004

**SAFe S = 0.55 ± 0.04 nM**

**SAFe D2 = 2.35 ± 0.19 nM**

The above average consensus values (and ± 1 standard deviation) were determined using data from samples that were either pretreated with a UV oxidation step or were analyzed by isotope dilution ICP-MS. In contrast the values listed below were from samples that were not pretreated with a UV oxidation step and that did not utilize isotope dilution. Data from lab L and M were omitted from the averages. It appears that a UV oxidation step or the use of isotope dilution may be necessary. There is still too much variation in the values for the SAFe D2 reference sample. More research needs to be performed evaluating the intensity and duration of the UV pre-treatment along with isotope dilution experiments.

**SAFe S = 0.47 ± 0.06 nM**

**SAFe D2 = 2.02 ± 0.17 nM**

With the data available, SAFe D1 appears identical to SAFe D2.

### References:

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6. Lohan, M.C., A.M. Aguilar-Islas, R.P. Franks and K.W. Bruland. Determination of iron and copper in seawater at pH 1.7 with a new commercially available chelating resin, NTA Superflow. *Analytica Chimica Acta*, **530**: 121-129 (2005).
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**Labs participating in the analysis of the SAFe reference samples to determine consensus values for dissolved Cu (listed in random order):**

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

Copper was concentrated by solvent extraction (Bruland et al., 1979) and subsequently analyzed by ICP-MS.

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

Concentrated off-line with the Mg(OH)<sub>2</sub> coprecipitation method (Wu and Boyle, 1997) and analyzed by ICPMS. Copper was analyzed using the ratio between the natural abundance of <sup>63</sup>Cu and an added <sup>65</sup>Cu spike. 1.6ml of sample and spike were allowed to equilibrate for several minutes. A single coprecipitation step was carried out followed by dilution of the precipitate with 4% HNO<sub>3</sub>. Blanks were quantified using 50 µl of low Cu seawater instead of 1.6ml.

**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).

**Ed Boyle (MIT, U.S.):**

400-bead NTA-type resin with isotope dilution ICP-MS. The 1.3 ml samples in 1.5 cc microcentrifuge tubes were spiked with <sup>65</sup>Cu, the solution pH was raised to 6 using ammonium acetate. The beads were added, and left to equilibrate overnight on a shaker table. The samples were centrifuged and supernatant siphoned off. The beads were washed/centrifuged/siphoned three times with high purity distilled water to eliminate salt. 150 µl of 0.1N HNO<sub>3</sub> was added

and allowed at least one day to release the Cd into the acid. The Cu 63/65 ratio was then determined by quadrupole ICP-MS using a low-flow micromist nebulizer.

**Michael Ellwood (Australian National U, Australia):**

Copper 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. Trace metal concentrations were determined by ICP-MS (820-MS Varian, Australia).

**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 isotope dilution ICP-MS. Prior to extraction the samples (12 mL) were UV oxidized and buffered to pH ~6.2.

**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 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 1.5M HNO<sub>3</sub> followed by detection with ICPMS.

**Jim Moffett (USC, U.S.):Here**

Isotope dilution ICP-MS

**Kathy Barbeau/Kristen Buck (SIO/UCSD, U.S.)**

ICP-MS using the method of Lohan et al. (2005).

**Kristen Buck (BIOS, Bermuda):**

Adsorptive cathodic stripping voltammetric method on UV-oxidized samples using the method of Buck and Bruland (2005).

The consensus values for the SAFe reference samples (yellow circles) compared with historical profiles from stations to the south (Bruland, 1980 – blue diamonds) and the north (Martin et al., 1989- red diamonds) of the SAFe station.

