Dissolved Copper – values in nmol/kg
Consensus values (± 1 std. dev.) for SAFe Reference Samples as of May 2013

SAFe S = 0.52 ± 0.05 nmol/kg

SAFe D2 = 2.28 ± 0.15 nmol/kg

SAFe D1 = 2.27 ± 0.11 nmol/kg

These are considered to be the consensus values of dissolved Cu for the SAFe Reference Samples as of May 2013. It appears that UV oxidation of samples is necessary for the methods that do not use isotope dilution to obtain an accurate value for dissolved Cu.

Labs participating in the analysis of the SAFe reference samples to determine consensus values for dissolved Cu:

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 $Mg(OH)_2$ coprecipitation method (Wu and Boyle, 1997) and analyzed by ICPMS. Copper was analyzed using the ratio between the natural abundance of ^{63}Cu and an added ^{65}Cu 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. Blanks were quantified using 50 μl of low Cu seawater instead of 1.6ml.
Yoshiki Sohrin (U. Kyoto, Japan):
Off line concentration using an EDTri-A-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 (Lee et al. 2011). The 1.3 ml samples in 1.5 cc microcentrifuge tubes were spiked with ^{65}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_3 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 (Milne et al. 2010). 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_3 followed by detection with ICPMS.

Dondra Biller/Ken Bruland (UCSC, U.S.):
Off-line extraction of UV-oxidized samples using Nobias PA-1 resin and ICP-MS (Biller and Bruland, 2012).

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

Christian Schlosser and Eric Achterberg (Plymouth, UK)
Off-line extraction using a WAKO chelating resin (Kagaya, 2009) followed by analysis on an Element XR ICP-MS. Samples were UV digested for 3 hours.

Rob Middag and Ken Bruland (UCSC, US)
Off-line extraction of UV-oxidized samples with Nobias PA-1 chelating resin and analysis on an Element XR ICP-MS Middag et al., submitted).

Maria Lagerstrom and Rob Sherrell (Rutgers University, US)
On-line flow injection with a modified seaFAST system, the Nobias PA-1 resin, isotope dilution and ICP-MS detection.

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