

## **Dissolved Cobalt – values in pmol/kg Consensus values ( $\pm$ 1 std. dev.) for SAFe Reference Samples as of May 2013**

**SAFe S =  $4.8 \pm 1.2$  pmol/kg**

**SAFe D2 =  $45.7 \pm 2.9$  pmol/kg**

**SAFe D1 =  $45.4 \pm 4.7$  pmol/kg**

These are considered to be the consensus values for the SAFe Reference Samples as of May 2013. It is clear that a UV oxidation step is necessary to determine the total dissolved Co in the reference samples. Concentrations determined on non-UV oxidized samples are roughly 60% of the value determined with adequate UV oxidation. 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. Older data sets for dissolved cobalt where samples were not UV-oxidized prior to analysis are not accurate.

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

#### **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.

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

Flow injection chemiluminescence method (Shelley et al., 2010) modified after Canizzaro 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 the Nobias PA-1 EDTri-A-type chelating resin with subsequent analyses by ICP-MS (Biller and Bruland, submitted) based upon the method of Sohrin et al. (2008). The method entails an eight column manifold enabling eight separate  $\sim$  40 mL samples to be processed simultaneously (Biller and Bruland, 2012).

#### **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 (Milne et al., 2010). 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 (Humboldt State University, U.S.):**

On-line flow injection of UV-oxidized samples 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 Nobias PA-1 EDTriA-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.

**Oliver Baars/Peter Croot (IFM-GEOMAR, Germany)**

Adsorptive cathodic stripping voltammetry with potassium bromate to catalytically enhance the signal (Baars and Croot, 2011).

**Johann Bown/Marie Boye/David Nelson (IUEM, Univ. Brest, France)**

Measurement by flow injection using an IDA chelating resin and chemiluminescence detection (Shelley et al., 2010) 48 hours after UV oxidation step.

**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 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, and ICP-MS detection.

**References:**

1. Shelley, R.U., B. Zachhuber, P.N. Sedwick, P.J. Worsfold, and M.C. Lohan. Determination of total dissolved cobalt in UV-irradiated seawater using flow injection with chemiluminescence detection. *Limnol. Oceanogr. Methods*, **8**: 352-362 (2010).
2. Bruland, K.W., R.P. Franks, G. Knauer and J. Martin. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel in seawater. *Analytica Chimica Acta*, **105**: 233-245 (1979).

3. Danielsson, L.G., B. Magnusson, and S. Westerlund. An improved metal extraction procedure for the determination of trace metals in seawater by atomic absorption spectrometry with electrothermal atomization. *Analytica Chimica Acta*, **98**: 47-57 (1978).
4. 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).
5. 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).
6. 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).
7. 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).
8. 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).
9. 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).
10. Milne, A., W. Landing, M. Bizimis and P. Morton. Determination of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in seawater using high resolution magnetic sector inductively coupled mass spectrometry (HR-ICP-MS). *Analytica Chimica Acta*, **665**: 200-207 (2010).
11. Biller, D.V. and K.W. Bruland. Analysis of eight trace metals in seawater using the Nobias-chelate PA-1 resin and magnetic sector inductively coupled plasma mass spectrometry. *Marine Chemistry*, **130/131**: 12-20 (2012).
12. Baars, O. and P.L. Croot. Comparison of alternate reactants for pM level cobalt analysis in seawater by the use of catalytic voltammetry. *Electroanalysis*, **22**: (2010).
13. Kagaya et al. A solid phased extraction using a chelate resin immobilizing ..., *Talanta*, **79**: 146-152 (2009).
14. Middag, R., K.W. Bruland and H.J.W. de Baar. GEOTRACES intercomparison of dissolved trace metals at the Bermuda Atlantic Time Series station. Submitted to *Limnology and Oceanography: Methods*.

