

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

SAFe S = 0.069 \pm 0.010 nmol/kg

SAFe D2 = 7.43 \pm 0.25 nmol/kg

SAFe D1 = 7.40 \pm 0.35 nmol/kg

The above concentrations are consensus values for the SAFe reference samples as of May 2013. The surface concentration was below the detection limit for some labs.

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

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

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

Dissolved Zn 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. Zinc was analyzed using the ratio between the natural abundance of ⁶⁴Zn and an added ⁶⁸Zn spike. Interferences from ⁶⁴Ni were monitored (using ⁶⁰Ni) and used to correct ⁶⁴Zn counts.

Deep samples: 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% HNO₃. Blanks were quantified by co-precipitating increasing volumes of deep seawater (300, 600, 900, and 1200 ul), and creating a regression line to calculate the 0 ml sample blank.

Surface samples: Double co-precipitation method (Wu, 2007).

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).

Michael Ellwood (Australian National U, Australia):

Zinc 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 concentration using an EDTri-A-type chelating resin with subsequent analyses by ICP-MS based upon the method of Sohrin et al. (2008). The method entails an eight column manifold enabling eight separate ~ 40 mL samples to be processed simultaneously (Biller and Bruland, 2012).

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

Off-line extraction using IDA Toyoppearl AF-Chelate-650 M 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.

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.

Jim Moffett (University of Southern California, U.S.):

Isotope dilution ICP-MS (reference?)

Derek Vance (Univ. of Bristol, UK):

Isotope dilution ICP-MS

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, 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).

Tim Conway and Seth John (U. South Carolina, US)

Off-line extraction by batch extraction using Nobias PA-1 chelating resin and analysis on a Neptune multi-collector ICP-MS for isotope ratios and concentrations using a double spike isotope dilution.

Jingfeng Wu (University of Miami, U.S.)

Mg(OH)₂ coprecipitation and analysis by isotope dilution ICP-MS (Wu and Boyle, 1997).

Taejin Kim and Hajime Obata (Atmosphere and Ocean Research Group, University of Tokyo, Japan)

Adsorptive cathodic stripping voltammetry after UV-oxidation with PDC as the added ligand.

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.

References:

1. 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).
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*, Vol. **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. 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).
5. 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).
6. 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**:2464-2470 (1997).
7. Wu, J. Determination of picomolar iron in seawater by double Mg(OH)₂ precipitation isotope dilution high-resolution ICPMS. *Marine Chemistry*, **103**: 370–381 (2007).
8. 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).
9. Kagaya et al. A solid phased extraction using a chelate resin immobilizing ..., *Talanta*, **79**: 146-152 (2009).
10. 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*.