

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

SAFe S = 48.0 \pm 2.2 pmol/kg

SAFe D2 = 27.7 \pm 1.5 pmol/kg

SAFe D1 = 27.7 \pm 2.6 pmol/kg

These are considered to be the consensus values for the SAFe reference samples as of May 2013. Labs have not noticed a significant difference between UV treatment and non-UV treated samples for dissolved Pb.

**Labs participating in the analysis of the SAFe reference samples to
determine a consensus value for dissolved Pb:**

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):

Lead 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) with hydrogen introduced into the collision reaction interface to reduce the interference of $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe .

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

$\text{Mg}(\text{OH})_2$ coprecipitation and analysis by isotope dilution ICP-MS (Wu and Boyle, 1997). Lead was analyzed by isotope dilution using the ratio between the natural abundance of ^{208}Pb and an added ^{204}Pb spike. Interference from ^{204}Hg was corrected by monitoring ^{202}Hg counts. 1.6ml of acidified 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_3 . Blanks were done using 50 ul of low Pb seawater instead of 1.6ml.

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 ^{204}Pb , 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 Pb into the acid. The Pb

206/204 ratio was then determined by quadrupole ICP-MS using a low-flow micromist nebulizer.

Jingfeng Wu (Univ. of Miami, U.S.):

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

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 (Biller and Bruland, submitted) 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 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.

Geoff Smith/Ken Bruland (UCSC, U.S.):

On-line flow injection analysis of 4 ml of sea water using an EDTri-A-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.

Matt Hurst (HSU, U.S.):

On-line flow injection using IDA Toyopearl AF-Chelate resin with analyses by ICP-MS (Hurst and Bruland, 2008).

Eric Achterberg (Plymouth Univ., UK):

Off-line extraction using IDA Toyopearl AF-Chelate resin followed by analysis using isotope dilution ICP-MS (Milne et al. 2010).

Celine Gallon, Cheryl Zurbrick and Russ Flegal (UCSC, U.S.):

On-line extraction using IDA Toyopearl AF-Chelate resin followed by analysis using isotope dilution ICP-MS (Ndung'u et al. 2003).

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).

Alan Shiller (University of Southern Mississippi, US):

Mg(OH)₂ precipitation with isotope dilution and ICP-MS.

References:

1. Lee, J-M, E.A. Boyle, Y. Echevoyen-Sanz, J.N. Fitzsimmons, R. Zhang and R.A. Kayser. Analysis of trace metals (Cu, Cd, Pb and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. *Analytica Chimica Acta*, **686**: 93-101 (2011).
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. 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. 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).
7. Wu, J., and E.A. Boyle. 1997. 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.
8. 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).
1. 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. Wu, J. 2007. Determination of picomolar iron in seawater by double Mg(OH)₂ precipitation isotope dilution high resolution ICP-MS. *Marine Chemistry*, **103**: 370-381.
10. Ndung'u, K., Franks, R. P., Bruland, K. W., and Flegal, A. R., 2003. Organic complexation and total dissolved trace metal analysis in estuarine waters: comparison of solvent-extraction graphite furnace atomic absorption spectrometric and chelating resin flow injection inductively coupled plasma-mass spectrometric analysis. *Analytica Chimica Acta* **481**: 127-138 (2003).
11. Kagaya et al. A solid phased extraction using a chelate resin immobilizing ..., *Talanta*, **79**: 146-152 (2009).
12. 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*.