

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

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A	0.067 ± 0.020		0.027 ± 0.004	0.013
		6.59 ± 0.11	0.09 ± 0.02	0.07
Lab B	0.05 ± 0.01	6.60 ± 0.33	0.008 ± 0.002	0.007
Lab C	0.09 ± 0.01	7.21 ± 0.25	0.09 ± .02	0.06
Lab D	0.07 ± 0.01	6.73 ± 0.39	0.058 ± 0.016	0.049
Lab E	0.075 ± 0.025	7.93 ± 0.08	0.05 ± 0.01	0.027
Lab F	0.058 ± 0.017	6.22 ± 0.28	0.113 ± 0.010	0.030
Lab G	< 0.07	7.26 ± 0.09		
Lab H	< 0.08	8.05 ± 0.36	< 0.08	0.08
Lab I	< 0.03	8.09	0.070 ± 0.018	0.054

**SAFe S = 0.068 ± 0.014 nM**

**SAFe D2 = 7.19 ± 0.70 nM**

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**SAFe D1 = 7.22 ± 0.62 nM**

The above concentrations are consensus values for the SAFe reference samples. The surface concentration was below the detection limit for labs G, H and I. The blanks and detection limits must be lowered in order to obtain a better value for the SAFe S concentration.

For the SAFe D2 reference sample there is a relatively large range of data reported (6.22 to 8.09 nM).

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

For SAFe D1 there is less data available (not shown), but the existing data for D1 is similar to D2.

### References:

1. 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).
2. 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).
3. 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).
4. 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).

5. 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).
6. Wu, J. Determination of picomolar iron in seawater by double Mg(OH)<sub>2</sub> precipitation isotope dilution high-resolution ICPMS. *Marine Chemistry*, **103**: 370–381 (2007).

### **Labs participating in the analysis of the SAFe reference samples to determine consensus values for dissolved Zn (labs listed in random order):**

#### **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)<sub>2</sub> coprecipitation method (Wu and Boyle, 1997) and analyzed by ICPMS. Zinc was analyzed using the ratio between the natural abundance of <sup>64</sup>Zn and an added <sup>68</sup>Zn spike. Interferences from <sup>64</sup>Ni were monitored (using <sup>60</sup>Ni) and used to correct <sup>64</sup>Zn 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% HNO<sub>3</sub>. Blanks were quantified by co-precipitating increasing volumes of deep seawater (300, 600, 900, and 1200 µl), and creating a regression line to calculate the 0 ml sample blank.

*Surface samples:* Double co-precipitation method (Wu, 2007). First co-precipitation uses 50ml of sample. The precipitate was dissolved in 0.5 N HCl, transferred to a Teflon conical vial and evaporated to dryness. 1.6ml of sample was added to the vial, followed by a second co-precipitation. Blanks were quantified by co-precipitating increasing volumes of a 1:1 mixture of surface:deep seawater (10, 20, 30 and 50 µl), and creating a regression line to calculate the 0 ml sample blank.

#### **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).

#### **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 EDTA-type chelating resin with subsequent analyses by ICP-MS based upon the method of Sohrin et al. (2008). The method entails a six column manifold enabling six separate ~ 75 mL samples to be processed simultaneously. The samples were UV oxidized for 1.5 hrs, amended with H<sub>2</sub>O<sub>2</sub> (final concentration of 10 µM), and adjusted to pH 6.5 with ammonium acetate prior to the concentration step. The resin columns were rinsed with a weak ammonium acetate buffer at a pH of 6.5 and eluted with 3 mL of 1 N nitric acid for a concentration factor of ~25, with subsequent analyses by ICP-MS. The Mo interference and correction were greatly reduced with the use of a PC3-SSI Peltier, water-cooled, spray chamber (Elemental Scientific Inc.).

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

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

**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.):**

Isotope dilution ICP-MS (reference?)

The figure below presents unpublished data from the SAFe station in fall 2004 (Jingfeng Wu's data from samples collected with the UAF Vane sampler) compared with historical data from a nearby station (Bruland, 1980). The consensus values for the SAFe reference samples are shown as evidence that the SAFe reference samples are representative of this station in the eastern North Pacific.

