

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

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A	2.40 ± 0.03	8.62 ± 0.12	0.048 ± 0.004	0.01
Lab B	2.20 ± 0.10	9.00 ± 0.41		
Lab C	2.46 ± 0.17	9.19 ± 0.24	< 0.01	0.01
Lab D	2.46 ± 0.07	8.45 ± 0.42		
Lab E	2.35 ± 0.04	8.43 ± 0.05	0.045 ± .012	0.04
Lab F	2.40 ± 0.13	8.90 ± 0.06	0.09 ± 0.01	0.02
Lab G	2.43 ± 0.05		< 0.01	0.02
Lab H	2.25 ± 0.06	7.93 ± 0.09	0.09 ± 0.01	0.03
Lab I	1.65	6.59	0.068 ± 0.020	0.060

**SAFe S = 2.39 ± 0.09 nM**

**SAFe D2 = 8.77 ± 0.31 nM**

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**SAFe D1 ~ 8.78 ± 0.29 nM**

These above concentrations are considered to be the consensus values for the SAFe reference samples at this time. The above average values (and ± 1 standard deviation) were determined using data from all labs except Lab H and I.

It appears that there is no significant difference between UV oxidized samples and non-UV treated samples.

For SAFe D1, less data is available (not shown), but it is similar to D2.

### References:

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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. Saito MA, J.W. Moffett, and G.R. DiTullio. Cobalt and nickel in the Peru upwelling region: a major flux of labile cobalt utilized as a micronutrient. *Global Biogeochemical Cycles* **18**:GB4030 (2004).
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).

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

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

Dissolved Ni was concentrated by solvent extraction (Bruland et al., 1979) and subsequently analyzed by ICP-MS.

**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):**

Dissolved Ni 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-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.

**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 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.

**Kristen Buck/Kathy Barbeau (SIO/UCSD, U.S.):**

Adsorptive cathodic stripping voltammetry on UV oxidized samples (Saito et al., 2004).

**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 figure below presents unpublished data from the SAFe station in fall 2004 (Bill Landing's data from samples collected with the CLIVAR rosette sampler) compared with historical data from a station located south of the SAFe Stn (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.

