

## Dissolved Lead – all values in pM – labs are anonymous

	<u>SAFe S</u>	<u>SAFe D2</u>	<u>Blank</u>	<u>Detect. Lim.</u>
Lab A	50 ± 2	29 ± 1		
Lab B	48.0 ± 0.7	27.4 ± 0.7	1.2 ± 0.1	0.4
Lab C	51.1 ± 2.6	29.4 ± 0.4	1.6 ± 0.3	1.0
Lab D	40.5 ± 1.2	25.3 ± 1.6	0.44 ± 0.16	0.5
Lab E	50.2 ± 3.5	27.0 ± 3.0		
Lab F	44 ± 1	25 ± 1		
Lab G	47.2 ± 1.7	31.4 ± 3.3		
Lab H	48.0 ± 0.5	27.6 ± 0.1		
Lab I	50.3 ± 1.0	28.5 ± 0.9	2.4 ± 1.3	4
Lab J	44.7 ± 1.2	27.5 ± 2.3		
Lab K	43.4 ± 1.0	25.7 ± 1.8	2.6 ± 0.1	0.4
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Lab L	20.5	29.8	4 ± 2	6

**SAFe S = 47.0 ± 3.4 pM**

**SAFe D2 = 27.6 ± 1.9 pM**

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**SAFe D1 ~ 26.0 ± 1.5 pM**

These are considered to be the consensus values for the SAFe reference samples at this time. The average values for the SAFe S and D2 (and ± 1 standard deviation) were determined omitting data of lab L.

Labs have not noticed a significant difference between UV treatment and non-UV treated samples for dissolved Pb.

Less data has been reported for SAFe D1 (data not shown), and it is similar to D2.

### References:

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3. 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).

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

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

**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):**

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 <sup>40</sup>Ar<sup>16</sup>O on <sup>56</sup>Fe.

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

Mg(OH)<sub>2</sub> 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 <sup>208</sup>Pb and an added <sup>204</sup>Pb spike. Interference from <sup>204</sup>Hg was corrected by monitoring <sup>202</sup>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<sub>3</sub>. 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. The 1.3 ml samples in 1.5 cc microcentrifuge tubes were spiked with <sup>204</sup>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<sub>3</sub> 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.

**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 8-hydroxyquinoline chelating 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.

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

Off-line extraction using IDA Toyopearl AF-Chelate 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. Mo interference on Cd is corrected by monitoring Mo during ICPMS analyses.

**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.

**Matt Hurst (HSU, U.S.):**

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

The figure below presents unpublished data from the SAFe station in fall 2004 (Ed Boyle and Jingfeng Wu's data from samples collected with the MITESS and UAF Vane sampler) compared with historical data from the deep water at a nearby station (Schaule & Patterson, 1976). 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. "Suspect" data are those in which contamination during filtration is inferred when "filtered Pb" is greater than "unfiltered Pb."

