

GEOTRACES Intercalibration Document

Date: 3 April 2016

Investigator: Alan M. Shiller; alan.shiller@usm.edu; 1-228-688-1178
Dept. of Marine Science, University of Southern Mississippi, 1020 Balch Blvd. Stennis Space Center, MS 39529 USA

Element(s): Dissolved molybdenum, reported in nmol/kg-sw.

Cruise(s): GP16 (US East Pacific Zonal Section).

Analytical Methodology:

Water column samples were taken from the GEOTRACES carousel and filtered through pre-cleaned, 0.2 μm Pall Acropak Supor filter capsules as described elsewhere (e.g., Cutter et al., 2012; Hatta et al., 2015). Near surface water samples were collected using an underway towed-fish pumped seawater system (Bruland et al., 2005) with samples filtered through sequential 0.45 μm Osmonics and 0.2 μm Polycarbonate (PCTE) cartridge filters. Filtered water was collected in 125 mL HDPE bottles (Nalgene) that had been pre-cleaned by soaking in hot 1.2 M HCl (reagent grade) for at least 8 h with subsequent thorough rinsing with ultrapure distilled deionized water (Barnstead E-pure). Samples were acidified in a laminar flow bench aboard ship using 0.5 mL of ultrapure HCl per 125 mL sample.

Molybdenum, along with Ba, was measured using a ThermoFisher Element 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) using an isotope dilution method similar to the one described for Ba by Jacquet et al. (2005). Aliquots (50 μL) of each sample were spiked with 25 μL of a 95Mo-enriched solution (~770 nM) and then diluted 30-fold with 0.2 μm ultrapure filtered water. A sample of 96.8% enriched 95Mo was obtained from Oak Ridge National Laboratories for use as the enriched isotope spike. The ICP-MS was operated in low resolution and both 95Mo and 98Mo were determined. The samples were bracketed every 10 samples with a blank and the spike 95Mo solution. The volumes of the spikes, samples and dilution water were accurately assessed by calibrating each pipette by weight. The reproducibility error of this method was estimated by comparing samples collected at the same depths on different casts at the same station. For 31 pairs of these replicate samples, the average absolute deviation was 2.3 nmol/kg or typically 2.1%. Repeated runs of runs of US GEOTRACES intercalibration samples and in-house reference solutions suggest a precision of $\pm 2.3\%$; the limit of detection for molybdenum was ~1 nmol/kg.

Intercalibration:

Table 1 lists intercalibration data for reference waters, both our results and results we were able to find in the literature. The only reported analysis of GEOTRACES intercalibration samples agrees well with ours. We also compare the salinity-normalized Mo results for several labs with ours. Note that some low Mo samples in hydrothermal and low oxygen areas were eliminated

from our average. The agreement is reasonable within the few percent precision usually reported for Mo.

Table 1. Molybdenum intercalibration data for reference waters; in nmol/kg-sw

Sample	USM	Goswami et al.	USM	Nakagawa et al.	Tuit & Ravizza	Firdaus et al.
GS	116.0 ± 2.8	116				
GD	112.0 ± 2.5	113				
Mean Seawater			108.7 ± 2.5	107 ± 7	107.6 ± 0.3	100 ± 3

Note: Mean seawater values are normalized to S = 35, except Firdaus et al.

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