Reply on RC3

Natalie R. Cohen et al.

Author comment on "Hydrothermal trace metal release and microbial metabolism in the northeastern Lau Basin of the South Pacific Ocean" by Natalie R. Cohen et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-96-AC3, 2021

The careful review by Reviewer #3 is much appreciated, and we are grateful for their effort in strengthening the geochemical aspects of this manuscript. We have specific responses to comments below. Importantly, we clarify that our dissolved metals "partial recovery" method using indium is technically a matrix correction, as indium is not introduced to the column prior to sampling binding, and instead is added into the elution acid. For the particulate metal analysis, indium is used as a proper internal standard, and is added to samples before the digestion. This has been clarified in the text. Specific comments are addressed below.

Line 125: Filters were not rinsed with DI to remove salts before freezing since the elements of interest do not require salt correction. It is possible low levels of dissolved metals on dried seawater were also included in the particulate analysis. This has been specified in the methods.

Line 134: Regarding the pH during sample loading, we followed the manufacturer's (Elemental Scientific) default guidelines in which acidified samples are mixed with concentrated and heavily buffered ammonium acetate (4M) of pH 6 at a 4:1 sample:buffer ratio, enabling sample loading onto the column at pH ~6 (Rapp et al., 2017; Wuttig et al., 2019). This is consistent with reports of complete column recovery from Nobias PA-1 resin for Fe, Mn, Ni, Cu, and Zn with a sample pH between 5.5-7 (Lagerström et al., 2013; Sohrin et al., 2008). Unfortunately, the pH of the waste was not checked, but we will do so going forward.

We tested the pH of a 4:1 acidified seawater sample:buffer mixture to simulate the seaFAST buffering step, which produced a pH of 5.5. Metal binding to WAKO resin at this pH shows similar performance to pH 6 for all metals apart from Mn, where binding (and count rates) increase with higher pH (Rapp et al. 2017).

Rapp et al. (2017) report a recovery of approximately 83.1 ± 2.6% for Fe with Nobias resin at a pH of 6.1, close to our assumed matrix correction of ~83% using In. Other metals with close corrections to ours include Cd (85.5 ± 3.1%) and Zn (95.0 ± 3.4). However, that study shows other metals with recoveries slightly larger (Cu: 102.7 ± 3.4%) or much lower (Ni: 38.5 ± 1.4%; Mn: 24.1 ± 0.2%), and if applied to our analysis, would suggest that our final concentrations are either artificially elevated or severely underestimated, respectively. We do not believe this was the case for Ni or Mn, as the

Geotraces GSC sample concentrations match consensus values (Table 1). It is possible our Cu concentrations are elevated compared to reference material and previously published studies partly due to underestimation of column recovery. We have included a note about this in the text.

Line 135: We did not test the difference in recovery between DI water and 1% nitric rinse solutions. A 1% nitric acid rinse solution was included in an early seaFAST protocol compiled by Kohler (2017), and was logical as we similarly flush between ICP-MS injections using a weak nitric acid rinse solution.

Line 147: We used a quartz cyclonic spray chamber (Thermo Scientific). This has been included in the text.

Line 155: We tested the reviewer's proposed recovery method using Geotraces reference material by subtracting out blanks from the measured GSC sample concentration, dividing by concentration factor, and dividing by GSC consensus values. We obtain the following averaged estimates (n = 3):

Fe: 89 +/- 6%

Mn: 82 +/- 5%

Ni: 81 +/- 8%

Cu: 108 +/- 11%

Zn: 76 +/- 19%

Cd: 87 +/- 8%

These are close to the average In matrix correction of 83% in our study, for all metals except Cu. It is possible that labile Cu concentrations increase over time in storage, and the consensus values are not reflective of this. We have included a note about this in the text to more clearly present this possibility to readers.

"It is possible that our higher dCu concentrations are a result of long-term acidified storage (8 years), during which time strongly binding refractory organic complexes could degrade and increase labile Cu (Little et al., 2018). Along these lines, Posacka et al. (2017) determined labile Cu concentrations in non-UV-oxidized seawater samples increase with storage time, with long term sample storage at low pH (>4 years) demonstrating similar concentrations to those UV-oxidized and measured within 2 months. Dissolved Cu has previously been reported as 3.1 nM in the deep southwest Pacific using Nobias-chelate PA1 resin (Takano et al., 2017), whereas the maximum raw dCu concentration we obtained in the southwest Pacific was approximately 4.2 nM. It is furthermore possible that the matrix corrections based on In are not reflective of Cu, which has been demonstrated to show both high (103%) and low (~50%) recoveries from Nobias resin at pH of 6.1 (Quéroué et al., 2014; Rapp et al., 2017). In addition, ArNa+ interferences on 63Cu cannot be completely ruled out given the abundance of Na+ in seawater (Diemer et al., 2002), although a cooled spray chamber was used to minimize such polyatomic interferences. The exact mechanism behind these elevated Cu concentrations is unclear at present, and an intercalibration exercise within the trace metal community using long-term stored seawater would be useful to further understand these offsets."

We have included a supplemental figure (attached) showing our St. 7, 8, and 9 compared to GP16 St. 36, which is the closest station to ours from the East Pacific Zonal Transect (EPZT) expedition (~ 1,000 km to the east). For example, here is how the deep (5 km)

concentrations (nmol/kg) compare between GP16 St. 36 (left) and Metzyme St. 8 (right):

Fe: 0.44,   0.65

Mn: 0.06, 0.13

Ni: 7.62, 8.06

Zn: 7.22,   7.72

Cd: 0.79, 0.85

Due to the potential storage-related issues with Cu, we are not directly comparing with GP16 data. The Fe and Cd concentrations are from John et al. (2017) and (2018) (https://www.bco-dmo.org/dataset/643809), and Zn, Ni, and Mn from the Bruland data set (https://www.bco-dmo.org/dataset-deployment/643427).

Line 175: It is possible $ArNa^+$ interfered with ^{63}Cu detection, which is known to occur with a seawater matrix containing high Na^+ (Diemer et al. 2002), although the column chemistry should remove most of the Na. This has been included as an additional mechanism possibly explaining our high Cu concentrations compared to consensus values.

Line 180: It is difficult to say with certainty which factors are responsible for the Cu offset between our data and previously published values. We believe the long storage time of over 8 years could have played a role in liberating labile Cu (Little et al. 2018, Pasacka et al. 2017). We have found the accurate quantification of Cu can be difficult as consensus values may not reflect long storage times, and the community may benefit from additional methodological comparisons. There has been recent discussion within the trace metal community regarding the accuracy of Cu methods applied to long term archives similar to the trends we have observed here.

Line 200: Regarding our claim that a fraction of Co is lost even after UV exposure, this is an unpublished finding that occurred during GEOTRACES intercomparison efforts. We have not published it since it involved other groups' data, but it is worth working with other authors on revisiting this since increasingly groups with ICP-MS datasets are submitting total dissolved and labile methods that are unverified and often not UV-irradiated making their interpretation and intercomparison difficult. Since these matters don't concern this study, we have deleted the sentence.

Line 210: We later determined that soaking acid-rinsed filter blanks in oligotrophic seawater for ≥1 week were effective at removing the background contamination, but this was years after the initial digestions were performed and the original batch of filters were not available. It was unlikely to be MQ contamination as this same MQ was used as seaFAST blanks, which were generally low in metal concentration. Indium was used to check recovery and was added with nitric acid prior to the digestion, serving as both an internal standard and matrix correction. Reference material was not used.

Due to high filter blank contamination, samples corresponding to pFe and pMn minimums largely within OMZs were selected from each of the three ICP-MS runs to serve as "blanks", and primarily to compare to the large pFe and Mn signals at St. 12. As a result these blanks are likely overestimated, making the resulting data conservative, but because particulate material in the upper water column is much higher than at depth, this is a relatively small conservative bias. Estimated "blank" concentrations were calculated by converting from cps to pM and scaling up based on In recovery. They are as follows:

St. 1, 3, 5, 6: Fe blank = 130 pM (St. 1 400 m). Mn blank = 5 pM (St. 5 800 m).

St. 10, 11, 12, 2, 7. Fe blank = 117 pM (St. 2. 450m). Mn blank = 3 pM (St. 2 225 m).

St. 4, 8, 9. Fe blank = 240 pM (St. 4 150m). Mn blank = 12 pM (St. 4 400m).

The text has been corrected to indicate the exact depths in which each blank is derived and estimated concentrations.

Our Milli-Q system is an Element system intended for low metal use. It has also been modified to not include the metal nut on the dispenser system, and instead uses a foot operated teflon tube dispenser.

Note: while calculating particulate metal blanks, we realized our dissolved metal blanks were not scaled to take into account the In matrix correction (they assumed no matrix effects). The corrected blank and LOD values are included in Table 2 (attached).

Line 299: There is a slight enrichment in dMn at St. 2 at approximately 200 m, where dCo reaches the highest concentrations and coincides with an oxygen minimum (Fig. 2&3). Dissolved Co distributions are more driven by biological influences, whereas the dMn distribution is strongly driven by Mn oxide photoreduction in surface waters and Mn oxidation at depth. More intense dMn signals have been observed elsewhere in OMZs due to inhibited Mn oxidation (e.g., Johnson et al., (1996), Lewis and Luther (2000).

Line 457: The exponential fit would be largely driven by one point, and we do not have enough data points to confidently suggest an exponential relationship, however this figure has been included for reference as a supplemental figure (attached).

"Fig. S6B: The relationship between dFe measured at St. 13 and [3]He from Lupton et al. (2004) shown in Fig. 5C alongside an exponential curve fit (in purple). Although the exponential fit is strongly supported by a high R2 value, it is largely driven by one data point."

Table 3: Depths that [3]He was measured by Lupton et al., (2004) were matched to the depths of dFe values obtained in this study. No upper water column [3]He values were available for 400-800 m, and they were therefore linearly extrapolated. In addition, He concentrations were not available in Lupton et al. (2004) and instead were estimated using nearby concentrations, at similar depths, from Jenkins et al., (2019). The ratios were obtained from the regression of dFe and [3]He individual sample points, not integrated. This has been clarified in the Table 3 caption.

Line 625: The InterRide Vents database includes polymetallic massive sulfides identified at vent sites in this region. At Eastern Lau Spreading Center vents, high metal concentrations suggest metal-sulfide formation during vent fluid mixing with background seawater, preventing sulfide oxidation by microbes (Hsu-Kim et al., 2008). If this similarly occurs in the NE Lau Basin, it could reduce sulfide availability to microbes. This has been included in the text.

"Metals and sulfide derived from vent fluid likely formed inorganic metal-sulfide clusters, reducing metal toxicity in the microbial community (Edgcomb et al., 2004) and limiting the bioavailability of sulfide to sulfide-oxidizing organisms, as observed in the Eastern Lau Spreading Center (Hsu-Kim et al., 2008; Sheik et al., 2015). Supporting this possibility, polymetallic massive sulfides have been observed in the NE Lau Basin (Beaulieu et al., 2013; Hawkins, 1986)."

Line 628: This was an important reference and has been included in the bacterial-mediated Mn oxidation discussion section.

"Lastly, heterotrophic Mn-oxidizing bacteria are a major conduit for Mn oxide precipitation in non-buoyant plumes (Cowen et al., 1990). Multicopper oxidase enzymes responsible for heterotrophic Mn oxidation in cultured hydrothermal bacteria (Dick et al., 2006), however, were not detected in the plume-influenced sample. Lithotrophic Mn oxidation is also theorized to occur in Mn(II)-rich vent fluids (Templeton et al., 2005) and has recently been described for the first time in Nitrospirae bacteria of tap water, which show high 16S rRNA sequence similarity to Nitrospirae from the Lo'ihi Seamount seafloor lava (Yu and Leadbetter, 2020). In this analysis, Nitrosopirae proteins were not enriched in distal plume-influenced seawater (>3 μm fraction), although proteins of this phyla were detected elsewhere in the transect. Genes expressed in Nitrospirae and hypothesized to play a role in lithotrophic Mn(II) oxidation, including outer membrane c-type cytochromes and porin-cytochrome c complexes (Yu and Leadbetter, 2020), were similarly not enriched. It is possible that environmental Mn oxidation proteins differ from those characterized in our reference databases, and are therefore missed during bioinformatic annotations."

All minor errors pointed out have been corrected.

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Please also note the supplement to this comment:
https://bg.copernicus.org/preprints/bg-2021-96/bg-2021-96-AC3-supplement.zip