

Biogeosciences Discuss., referee comment RC3
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Comment on bg-2021-96

Anonymous Referee #3

Referee 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-RC3>, 2021

General comments

The work presented by Cohen et al represents a significant contribution to scientific progress in the field of marine biogeochemistry which is within the scope of this journal. The study combines cutting edge metaproteomic with trace metal measurements representing a rare combination of detailed biological and geochemical data which is needed to further progress our understanding linkages between ocean biogeochemical cycles and microbial ecology. Several new ideas are suggested such as deep-sea organisms exploiting gradients in trace metals via metabolic plasticity, differences in transport proteins between distal hydrothermal plume and background samples reflecting utilisation of or protection from metals by deep-sea micro-organisms and the unexpected presence of proteins associated with photosynthetic processes mainly belonging to *Prochlorococcus*, either as a result of cell maintenance or present as degraded cells.

The scientific approach is valid, however comment the biological analysis is outside of my area of expertise. I have concerns about the use of the internal standard diluted in the elution acid (Indium) as a method of measuring the recovery of metals extracted from samples as they are loaded onto the chelating column. I would like to see further proof that this is a valid method of assessing and correcting for any losses in sample recovery. The pH at which the samples were loaded onto the column should be stated as this is the main control on recovery of metals from a seawater sample. I would also like to know if there were any checks performed on the recovery of metals from the filters? And further detail on the filter blank value used. The data looks oceanographically consistent and results for reference standards are broadly in agreement with consensus values, but I think addressing these points in the methods text more clearly is important for publication. Please see the specific comments on this section.

The data and manuscript are written in a clear and concise manner with appropriate well-presented figures. I have made minor suggestions for improving several figures/tables as well as adding references. In particular I found the results & discussion of the

metaproteomic and microbial community data easy to understand and follow despite not being entirely familiar with this analysis. Well written discussions and presentation of this kind of data are key in papers like this one to bridge the disciplinary gap between ocean geochemistry and biology to bring a combined understanding within the ocean research community.

Specific comments

Line 20: Should this read "long range transport of trace metals"

Line 33: There are other studies that can be referenced that describe an overview of nutrient limitation e.g. J.K. Moore et al 2001 or C.M Moore et al 2013

Line 55: also reference Saito nature geoscience paper that looks at this

Line 58: While Bennet et al is a corner stone citation for this work there are more recent papers by J. Hawkes that use more robust methods.

L206: Supor is the brand name, it should mention that they are made of polyethersulferone (PES)

Line125: Were the filters rinsed with DI water to remove salts before freezing?

Line 134: If the ammonium acetate buffer had a pH of 6 then this would have resulted in a pH lower than 6 during sample loading when the buffer is mixed with the sample with pH <2. Which would explain the sub-optimal recovery of metals. Unless this is meant to say the samples were passed over the column at a pH of 6? Its always useful to check the pH of the waste from the seaFAST system to measure the pH of sample loading onto the column directly.

Line 135: Interesting that you used a 1% nitric acid rinse, was this more effective than DI water or dilute ammonium acetate used in other studies?

Line 142: Its worth bearing in mind that the Milli-Q water will also carry a small blank however this is still the best way to estimate the blank contribution.

Line147: What was the make/model of spray chamber/inlet system used?

L155: This isn't a great way to estimate recovery as most of the In will pass over the resin column at pH <2 as its diluted in the acid, in comparison to the samples when loaded onto the column at pH 6. It also won't account for any metals lost during the rinsing stage.

Wouldn't a better way to estimate recovery be to compare the values obtained for the

GSC reference seawater against the consensus values? I appreciate that this only gives recovery for those standards and that the In calculation maybe necessary to calculate recovery for each individual sample, but perhaps a comparison of values obtained for GSC vs consensus values to show whether or not you get a similar estimate of recovery as using the In calculation? This would help to validate the approach of checking recovery in this manner which I haven't seen before. I can see that most of the numbers in Table 1 are higher than the consensus values so it's possible applying this In correction may have over corrected the values (with the exception of Zn which as you mention is more contaminant prone and trickier to measure).

Another way to add some reassurance on the data quality here is to add additional columns to Table 1 comparing the average and stdev of deep ocean water concentrations measured on this section to the nearby GP13 section which has similar concentrations of macronutrients in deep waters.

Loading pH can be checked by adding the buffer and a sample together in the same mixing ratio as the seaFAST to check the pH and compare that pH to the elution profiles in the paper by Rapp and estimate recovery based on the elution profiles in that paper to see if this agrees with the 83 % In estimate.

L175: these measurements were performed on a collision cell iCAPQ and most of the data from the consensus values were likely measured on a sector field ICP-MS, could interference elements also have caused this?

L180: The sharing of consensus values is designed to intercalibrate lab results. The Cu value in table 1 is 1.36 times higher than the consensus value, if I multiply the previously measured dCu by Takano et al 2017 of 3.1 nM I get 4.2 nM which is what is measured here. Is this not evidence of a systematic offset in either this data or that of Takano et al 2017?

L200: Is there a reference for this claim that a fraction is lost even after UV exposure? If the Co data has already been published previously you should state this clearly here.

L210: Can this procedure not be repeated in the lab by cleaning some more filters and rinsing them with seawater? What is the value from the 400 m OMZ sample used as a blank, this should be stated clearly here. Were there any reference materials dissolved in acid to check recovery of the acid digestion procedure. Encase its useful for future reference I have experienced contamination from Milli-Q water systems in the past as most models have a metal knut where the filter screws into the end of the dispenser and this can rust over-time.

L215: I defer to the experience of the other two reviewers on this part of the analysis as this is not my area of expertise.

L269: suggest upper is changed to Northern

L272: scavenging also includes aggregation of colloidal particles

L299: Then shouldn't there also be an increase in dMn in the same area?

Fig 3: Add latitude to Zn* plot, interesting that there doesn't appear to be an increase in Zn* at stn 1 associated with Lohi signal as Roshan et al observe in their paper on the east pacific rise plume but this is observed at station 13. Perhaps a result of the different venting styles.

Line 362: provide reference for vent fluid geochemistry please

Fig 5b: The text would be easier to understand if the predominant direction of water mass movement at 2000 m as an arrow to the map?

L407: because it would require intense upwelling?

L457: Looks like a polynomial regression could also fit to the Fe data and get a similar or improved r^2 value. Either show both or give justification statistically for showing the linear trend fits better for Fe.

Table 3. When it says the ^3He data is extrapolated do this mean the He was matched the sampling depths up with the metzyme sampling depths using the profile shape? That's fine if so but it needs explaining clearer rather than just saying it was extrapolated. Also are the ratios obtained from regression of integrated Fe and He data or regression though individual sample points? Im guessing individual samples but worth stating to be clear as other studies use both or one/other e.g Resing and Fitzsimmons papers in nature/nature

geoscience.

L625: Is there an excess of sulphide relative to metals in Lau Basin vent fluids, or are metals present in greater concentrations in which case a lot of free sulphide might be consumed by metal-sulphide mineral precipitation? This data should be available from the InterRidge data set for the vents on your map.

L628: This paper by Hang seems relevant here
<https://www.nature.com/articles/s41586-020-2468-5>

L677: might be better to say "similar rather than "rivals"?"

Technical Corrections

Line 43: include not including?

Line321: started sentence with lowercase letter dCd

Line 329: upregulation of