Clim. Past Discuss., 11, C842–C858, 2015
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Climate of the Past
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Interactive comment on "Trace metal evidence for a poorly ventilated glacial Southern Ocean" *by* M. Wagner and I. L. Hendy

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Received and published: 26 June 2015

Firstly we thank Anonymous Referee #2 for his or her detailed comments. We do, however, wish to defend our interpretation of the trace metals and stress the importance of introducing ideas and new data to the community for evaluation. With regard to glacial-interglacial changes, since the groundbreaking work of Kumar et al. (1993), paleoceanographers have found that marine productivity changes in the Southern Ocean are more nuanced than weight % TOC or biogenic silica can resolve alone. Interpretation of Southern Ocean productivity has become more sophisticated over time as additional proxies are measured. We now know that there are changes in the community structure of primary producers which in turn impact changes in the export productivity (e.g., Abelmann et al., 2006; Anderson et al., 2009). These shifts relate to changing environmental conditions such as sea ice cover, micronutrient availability, and wind structure. In our manuscript we present new redox-sensitive trace metals as proxies that allow us to peel back another layer of Southern Ocean paleoceanography, giving us more sophisticated insight into bottom water and sediment geochemistry. We are not re-interpreting previous studies of Southern Ocean marine productivity or implying that they are incorrect. We are taking knowledge gained by proxy development in other highly productive oceanic regions and applying them to the Southern Ocean to clearly demonstrate that bottom and pore water geochemistry changed dramatically between the LGM and the modern ocean.

Below please find our responses to the specific and technical comments.

Specific comments:

Section 4.1

1. We mistakenly omitted the references to the figures. We will fix this in a revised manuscript.

2. The U and other data from Anderson et al. (2009) are freely available from the NOAA Paleoclimatology database. We are including a figure (Figure R2-1) with this response that plots U fluxes and concentrations alongside our trace metal data. The U data were not included in the original figures because the associated reference in the text is a very minor part of the manuscript.

Section 4.2

1. As we state in Section 2, no quantitative relationship between trace metal accumulation and export production or bottom water ventilation has yet been established. Neither has a linear relationship among trace metals been established. This is probably an unreasonable expectation given that every proxy has its own set of biases that vary with different environments at the sediment-water interface. Hence we rely on concentrations of productivity proxies (Ag and Cd; also Corg and Sibio, see below) versus Re

and Mo to establish the relative importance of bottom water oxygenation versus export production. Silver and Cd have previously been utilized as reliable recorders of export production (e.g., Rosenthal et al., 1995; Hendy and Pedersen, 2005; Dean et al., 2006; Chang et al., 2014). It is not uncommon to compare changes in productivity proxies to changes in redox-sensitive trace metals to understand temporal changes in bottom water ventilation versus export production (e.g., Ivanochko and Pedersen, 2004; Hendy and Pedersen, 2005; McKay et al., 2005). We base our argument of decreased LGM bottom water oxygen concentrations on the following:

1) Decreased delivery of Ag and Cd to sediments resulting from lower biogenic particle flux should result in decreased sedimentary Ag and Cd concentrations (see Section 2.1 describing trace metal geochemistry).

2) If increased/decreased oxidant demand due to increased/decreased organic matter delivery to sediments affected sedimentary redox conditions, trace metals reflecting productivity (Ag and Cd) and those that diffuse along concentration gradients into sediments (Re and Mo) would be expected to show similar behavior (e.g., MIS 1 and 3, Chang et al., 2014). Although this pattern is observed above ∼205 cm, correlations among Ag, Cd, and Re in particular (we interpret Mo to reflect primarily association with Mn oxyhydroxides) are less good below ∼205 cm. For example–although we do not highlight this in this manuscript–Re concentrations decrease at 330 cm while Ag and Cd concentrations are increasing. Furthermore, between 261-309 cm, Re concentrations vary by only ∼6% (in other words, the profile is relatively flat), whereas Ag concentrations decrease by ∼60% and Cd concentrations by ∼72%. This incoherence suggests a more complicated scenario of decreased bottom water O2 concentrations and elevated export production especially before ∼205 cm (∼21 ka). For the purposes of the paper and the ideas we wanted to put forward, we chose to focus on the LGM (∼20 ka).

Additionally, correlations among the trace metals are very strong for TN057-13-4PC, but not for RC13-254 where Ag and Cd are strongly correlated to one another, but not to Re and Mo (see correlation tables).

3) Trace metal concentrations similar to those of glacial RC13-254 are found in modern sediments underlying coastal upwelling regions with oxygen-depleted bottom waters and high surface productivity (e.g., parts Arabian Sea, Morford and Emerson, 1999; Chile margin, Böning et al., 2005; parts Mexican margin, McKay and Pedersen, 2008; Nameroff et al., 2002). Weight percent organic carbon in sediments at these locations tends to be higher (~2-4% along the Mexican and Chile margins) than what is observed at site RC13-254 (generally < 1 wt. %). We find it implausible that enhanced export production alone during the last glacial period can adequately account for the 10- to 100-fold increases in Ag, Cd, and Re concentrations observed clearly in RC13-254. We know of no prior studies that document such a large effect of export production on trace metal accumulation in sediments underlying highly oxygenated bottom waters. In a revised manuscript, we aim to clarify this point that we made in the original manuscript from page 11, line 23 to page 12, line 2.

4) A new paper that was published shortly after we submitted our manuscript implicates the Southern Ocean as a source of deep waters present off the Portuguese margin that were oxygen depleted at the LGM by ~45 μmol/kg (Hoogakker, B. A. A., Elderfield, H., Schmiedl, G., McCave, I. N., and Rickaby, R. E. M.: Glacial-interglacial changes in bottom-water oxygen content on the Portuguese margin, Nature Geosci, 8, 40-43, 2015).

5) We acknowledge that we did not utilize the Corg and Sibio records as much as we could have to support our case, and we will incorporate these records in a revised manuscript. During the LGM, very little change is seen in Corg concentrations (Figure 3) or fluxes (Figure S1) in RC13-254 although Re concentrations increase greatly (Figure 3). Biogenic silica (opal) fluxes appear to increase slightly and then decrease (Figure 3), but resolution is very low for these data. These productivity proxies, therefore, do not indicate a sufficient increase in export production that could have consumed sedimentary oxidants and led to an increase in Re concentrations. There are two other

parts of the core where Re and productivity proxies appear to decouple. At 330 cm, Re concentrations drop suddenly without corresponding changes in Corg (concentrations or fluxes), Ag, or Cd. The sample at 330 cm, as well as the samples before and after, was re-run to verify the results obtained–the values are real. The other example occurs at 220-240 cm, where the productivity proxies Ag, Cd, and Corg all increase, but Re is essentially unchanged. These several instances where the proxies disagree are what led us to suspect a dual influence of bottom water oxygen contents and export production prior to deglaciation. More data–and higher resolution data–in future studies are certainly required to solidly establish this phenomenon, but we require a starting place and our results provide a platform for future investigation.

6) Within the limits of the age model at RC13-254, an increase in sedimentation rate (Figure R2-2) from 16 cm/kyr to 38 cm/kyr is not detectable until ∼170-180 cm (∼18-19 ka), at which time a deglacial increase in productivity appears to begin. There is also no indication that terrigenous input should have led to increases in Re concentrations at the LGM (Figure 3g). Similarly at TN057-13-4PC, sedimentation rates are 11 cm/kyr until ∼730-760 cm/kyr (∼14-16 ka) when they increase to 53 cm/kyr in response to reinvigorated upwelling and biogenic silica production (Figure 4f; Anderson et al., 2009). Terrigenous input also drops rapidly just before upwelling resumes (Figure 4g).

Additional examples are available where productivity proxies decouple from redox proxies. Morford et al. (2001) suggest that a decrease in bottom water renewal in Saanich Inlet (along with perhaps an increase in diatom productivity) during late deglaciation may have caused a Re/Al peak that had no corresponding U/Al or Cd/Al peak. These authors furthermore point out that the bottom waters were oxic at this time, although oxygen must have been depleted in the top centimeter or less of pore waters. Nameroff et al. (2004) infer a decrease in bottom water ventilation (eastern tropical North Pacific) from Re data and estimate that productivity would need to change by an order of magnitude in order to induce a comparable effect in trace metal accumulation as ventilation changes. Productivity proxies and trace metals have also been shown to decouple along the Chile margin (oxygen decrease after deglaciation; Muratli et al., 2009) and the California margin (oxygen increase with no reduction in productivity during deglaciation; Hendy and Pedersen, 2005).

2. The peaks referred to for TN057-13-4PC were always somewhat anomalous. Comments from referee #1 pointed out that enhanced delivery of lithogenic material to the sediments at this time could have significantly affected trace metal concentrations, and we are prepared to modify our interpretation accordingly for this part of the core. We originally cropped the figures because otherwise it was impossible to see the other features of the trace metal record using a larger scale. However, splitting the axes is a good idea that we had not considered before, and we are happy to plot the figures this way in a revised manuscript.

3. The comment about spatial heterogeneity referred to water chemistry, and specifically to oxygen contents. The question asked is a difficult one to answer, although we note that in general we agree with previous studies that have found a northward shift of the high productivity zone during the last glacial period (Section 4.4). There is currently no quantitative way to translate trace metal concentrations into estimates of organic matter flux to the sediment-water interface. Trace metal concentrations can have biogenic, lithogenic, and authigenic components. Assessing organic carbon flux across the Antarctic and Subantarctic Zones would require adequately accounting for the lithogenic component, which can be done in various ways but all have some disadvantage. Also, the trace metal record at RC13-254 has been compromised in the upper part of the core due to burndown, complicating any comparison of the cores. Productivity in the Southern Ocean has been very well addressed by many previous studies, and we feel it would be an over-interpretation to discuss what the relative magnitudes of the trace metal concentrations mean for carbon flux across the Southern Ocean.

4. The core tops may be disturbed (i.e., the organic carbon concentrations are artifacts of coring) and data from this interval should be viewed with suspicion until checked against data from the trigger weight core or multicore. Additionally, relatively fresh

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organic carbon is possibly still being degraded by microbes. In either case, we do not wish to draw meaning for the coretop organic carbon samples and their relationship with trace metals.

Section 4.3

1. I (Wagner) checked the data files I have. It looks like the first data point for the correlation with the North Atlantic site is in the 13.5-14.0 ka bin. It is difficult to know exactly where to begin excluding the burndown region, but the referee is correct that if this data point is excluded the correlation becomes poorer. The next data point is in the 14.5-15 ka bin. However, the first data point (where both Re and ventilation age have values) for the South Atlantic site is actually in the 17.0-17.5 ka bin, well out of the burndown region, and so this correlation still holds. This was not meant to be intentionally misleading; we thank the reviewer for noticing this discrepancy. Regardless, it is unclear which data points are best included in such a comparison. Even without a quantitative comparison, the similar patterns of Re concentrations and ventilation ages raise the possibility that these proxies are responding to the same water chemistry–poorly ventilated waters would tend to increase both the ventilation age and Re accumulation in the sediments. If the correlations are problematic, they can be removed. We are including a new figure that shows 3-point moving averages of the ventilation ages from the North and South Atlantic sites, and the Re data and organic carbon data from RC13-254 (Figure R2-3). The data were smoothed to highlight the overall pattern: increasing ventilation age and Re values (more isolated waters) toward the LGM, then decreasing values (less isolated waters) during early deglaciation, and a steep dropoff ∼15 ka. Renewed bottom water oxygenation should decrease sedimentary Re accumulation, trigger burndown, and create “younger” bottom waters, all consistent with the available data. Burndown and/or a slowdown in organic matter delivery to the sediment-water interface could have contributed to the decrease in organic carbon concentrations ∼15 ka.

2. We believe the data demonstrate an important and complementary role for bottom

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water oxygenation during the last glacial period (see responses above). Hence the discussion of water mass restructuring is not an over-interpretation of the data.

Technical corrections:

1. Resolution mode: Low resolution mode was used on the Element. Molybdenum and Cd separation: 0.5 M HCl was first introduced to the column before loading the sample. Silver and Cd will remain on the column while a chloride ion is present, but Mo will not. Silver and Cd were then eluted from the column using 4 M HNO3. The method for digesting and preparing trace metal samples was developed in Tom Pedersen's lab perhaps 20 years ago. Some of the details relating to Ag are available in Kathleen Gordon's M.Sc. thesis, which can be accessed through the University of British Columbia's cIRcle website. Details for the other trace metals are found in Tara Ivanochko's M.Sc. thesis (University of British Columbia) and Stephanie Kienast's Ph.D. thesis (University of British Columbia). Multiple published articles have been produced from the thesis work. For this study, trace metal concentrations for the sediment standard MESS-3 were acceptably accurate (see table below). Batches with unacceptable concentrations for standards were re-run. Unfortunately, this did require re-running one large batch. Oxide production: Zirconium and Nb oxides are known to interfere with Ag; these are effectively removed by the column. I (Wagner) checked this and other potential interferences when setting up the method in Dr. Hendy's lab, and the procedure for Ag is referenced both in Kathleen Gordon's thesis and in Jennifer McKay's Ph.D. thesis (University of British Columbia). Molybdenum oxide interferes with 111Cd, but Mo and Cd were separated by the column. Rhenium has no polyatomic interferences (May and Wiedmeyer, 1998). BrO+ species potentially could interfere with Mo isotopes, but Br- is oxidized to volatile Br2 during the digestion process and is lost (Zheng, 1999; Columbia University, Ph.D. thesis). Other oxide species were negligible and were minimized by proper tuning of the ICP-MS prior to analysis.

2. We have made a second map for Figure 1 (Figure 1_R2) that now shows all cores mentioned in the manuscript.

Interactive comment on Clim. Past Discuss., 11, 637, 2015.

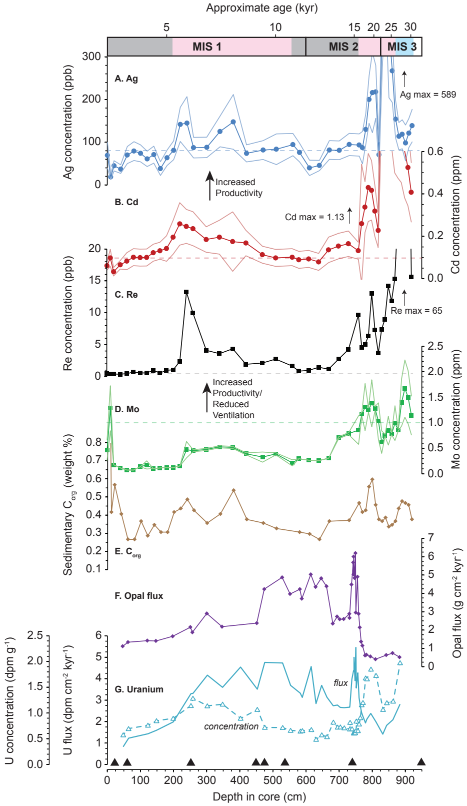

Figure R2-1

Fig. 1. Figure R2-1

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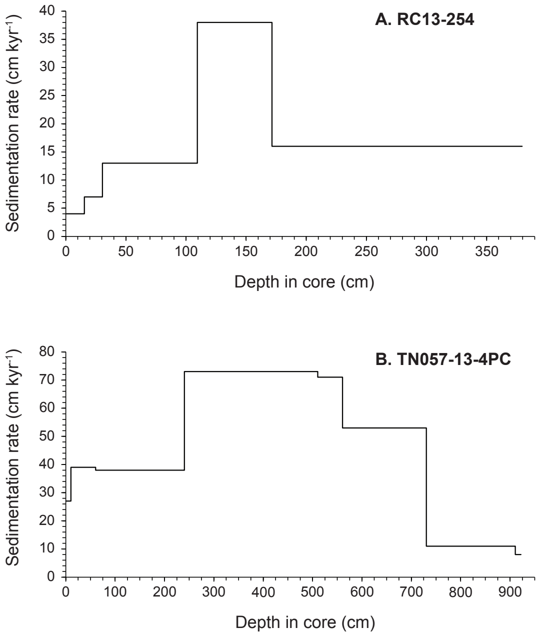

Figure R2-2

Fig. 2. Figure R2-2

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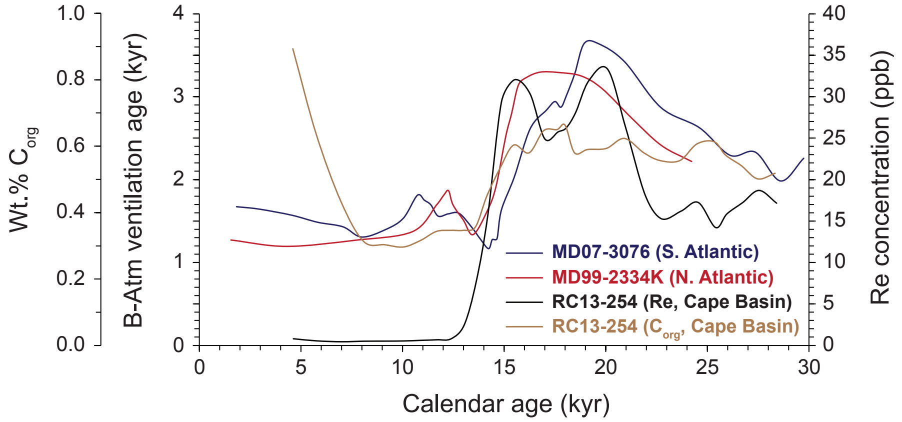

Figure R2-3

Fig. 3. Figure R2-3

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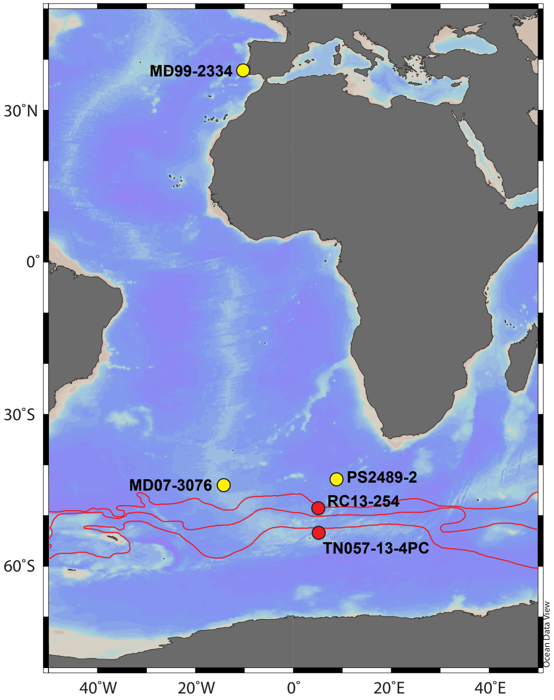

Figure 1_R2

Fig. 4. Figure 1_R2

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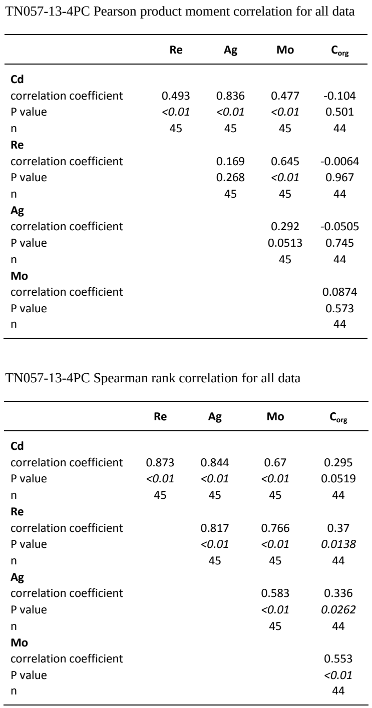

TN057-13-4PC Pearson product moment correlation for all data

	Re	Ag	Mo	C_{org}
Cd				
correlation coefficient	0.493	0.836	0.477	-0.104
P value	*<0.01*	*<0.01*	*<0.01*	0.501
n	45	45	45	44
Re				
correlation coefficient		0.169	0.645	-0.0064
P value		0.268	*<0.01*	0.967
n		45	45	44
Ag				
correlation coefficient			0.292	-0.0505
P value			0.0513	0.745
n			45	44
Mo				
correlation coefficient				0.0874
P value				0.573
n				44

TN057-13-4PC Spearman rank correlation for all data

	Re	Ag	Mo	C_{org}
Cd				
correlation coefficient	0.873	0.844	0.67	0.295
P value	*<0.01*	*<0.01*	*<0.01*	0.0519
n	45	45	45	44
Re				
correlation coefficient		0.817	0.766	0.37
P value		*<0.01*	*<0.01*	*0.0138*
n		45	45	44
Ag				
correlation coefficient			0.583	0.336
P value			*<0.01*	*0.0262*
n			45	44
Mo				
correlation coefficient				0.553
P value				*<0.01*
n				44

Fig. 5. correlation tables page 1

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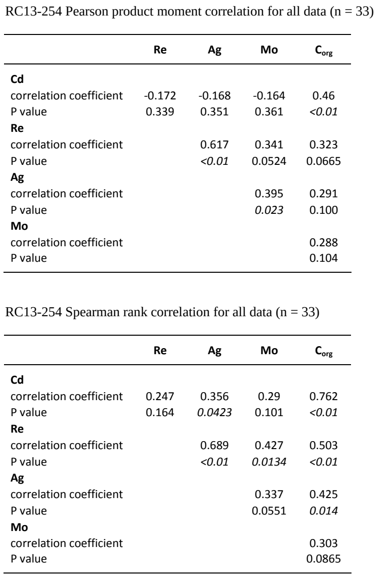

RC13-254 Pearson product moment correlation for all data (n = 33)

	Re	Ag	Mo	C_{org}
Cd				
correlation coefficient	-0.172	-0.168	-0.164	0.46
P value	0.339	0.351	0.361	*<0.01*
Re				
correlation coefficient		0.617	0.341	0.323
P value		*<0.01*	0.0524	0.0665
Ag				
correlation coefficient			0.395	0.291
P value			*0.023*	0.100
Mo				
correlation coefficient				0.288
P value				0.104

RC13-254 Spearman rank correlation for all data (n = 33)

	Re	Ag	Mo	C_{org}
Cd				
correlation coefficient	0.247	0.356	0.29	0.762
P value	0.164	*0.0423*	0.101	*<0.01*
Re				
correlation coefficient		0.689	0.427	0.503
P value		*<0.01*	*0.0134*	*<0.01*
Ag				
correlation coefficient			0.337	0.425
P value			0.0551	*0.014*
Mo				
correlation coefficient				0.303
P value				0.0865

Fig. 6. correlation tables page 2

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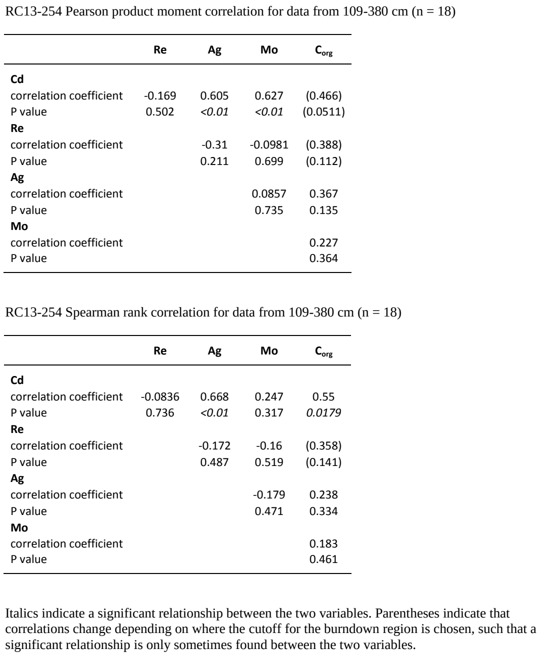

RC13-254 Pearson product moment correlation for data from 109-380 cm (n = 18)

	Re	Ag	Mo	C_{org}
Cd				
correlation coefficient	-0.169	0.605	0.627	(0.466)
P value	0.502	*<0.01*	*<0.01*	(0.0511)
Re				
correlation coefficient		-0.31	-0.0981	(0.388)
P value		0.211	0.699	(0.112)
Ag				
correlation coefficient			0.0857	0.367
P value			0.735	0.135
Mo				
correlation coefficient				0.227
P value				0.364

RC13-254 Spearman rank correlation for data from 109-380 cm (n = 18)

	Re	Ag	Mo	C_{org}
Cd				
correlation coefficient	-0.0836	0.668	0.247	0.55
P value	0.736	*<0.01*	0.317	*0.0179*
Re				
correlation coefficient		-0.172	-0.16	(0.358)
P value		0.487	0.519	(0.141)
Ag				
correlation coefficient			-0.179	0.238
P value			0.471	0.334
Mo				
correlation coefficient				0.183
P value				0.461

Italics indicate a significant relationship between the two variables. Parentheses indicate that correlations change depending on where the cutoff for the burndown region is chosen, such that a significant relationship is only sometimes found between the two variables.

Fig. 7. correlation tables page 3

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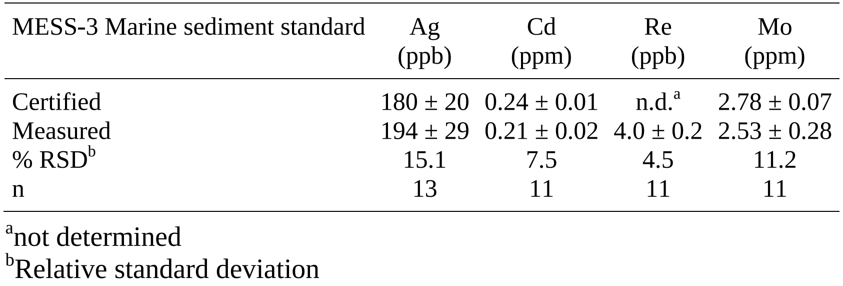

MESS-3 Marine sediment standard	Ag (ppb)	Cd (ppm)	Re (ppb)	Mo (ppm)
Certified	180 ± 20	0.24 ± 0.01	n.d.[a]	2.78 ± 0.07
Measured	194 ± 29	0.21 ± 0.02	4.0 ± 0.2	2.53 ± 0.28
% RSD[b]	15.1	7.5	4.5	11.2
n	13	11	11	11

[a] not determined

[b] Relative standard deviation

Fig. 8. MESS-3 values