

Interactive comment on “Manganese incorporation in living (stained) benthic foraminiferal shells: A bathymetric and in-sediment study in the Gulf of Lions (NW Mediterranean)” by Shauna Ní Fhlaithearta et al.

Anonymous Referee #2

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This manuscript aims to understand Mn incorporation into benthic foraminifera and explore its potential use for reconstructing pore water redox condition and organic matter content of sediments. Although the topic is potentially very interesting I have serious concerns about the analytical side of Laser ablation measurements. The authors should clarify these issues before ‘interpretation/discussion’ part of the manuscript can be evaluated. Therefore, I recommended major revision for this work. Below, I summarised the questions for the analytical part of the work.

1- Detection limits for Mn/Ca measurements. Mn values in ontogenetic (i.e. not altered)

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foraminiferal calcite is very low ($\mu\text{mol}/\text{mols}$) which make it challenging to accurately quantify with laser ablation measurements. Usually in our lab we use large laser spot size and energy to get sufficient signal to noise ratio (>100). The authors in this study provided very basic description of analytical procedures in the method section, which overshadows the result and discussion as there is no assurance on the quality of the measurements. The main concern I have is lack of any estimation on detection limits of their method. Fig 2 shows typical ablation profile BUT the Mn signal to noise ratio is very low (<10). Such low noise to signal ratios usually correspond to very noisy measurements (large error bars), which in fact is a common feature of the data presented in this work (figs 5,6,7). In fig 6a, there are labels 'LD' which I presume indicate detection limits and they are $1\mu\text{mol}/\text{mol}$. If this is true detection limit then majority of the data presented in this work (in exception of data for Melonis) has very little analytical base. Simply it is too close to detection limits compared to error bars and therefore statistically indistinguishable from noise. The authors should really accurately estimate their errors in the background ($\text{LD} = 2\text{SD}$ of the variance in the background signal) and also variance in the signal itself. This is crucial for interpretation of the data. For example, the summary in fig 7 as it presented now shows no trends as the errors are huge and horizontal line is the best solution for these plots. Note, if $1\mu\text{mol}/\text{mol}$ is the detection limit, then more than 60% of the data is within the error bar from the noise.

2- Inappropriate standards for calibration. The authors used NIST610 for Mn/Ca calibration. This standard has $\sim 400\text{ppm}$ of Mn, which is $>10,000$ times higher than typical foraminifera values. It is advisable to use Nist 612,614 pair for this kind of application to avoid artefacts/noise in calibration. The typical LA-ICPMS will give 3-5% reproducibility on NIST glass. Considering that calibration is one point calibration and $0=\text{blank}$, the 5% variability at 400ppm will result in large variance at few ppbs level. Considering very low noise/signal ratio (see above) all propagated errors will case huge variance in the resulting data. I am afraid this has to be fixed before discussing the science behind Mn incorporation into foraminifera.

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Minor comments

- Measurements in the lab should be validated by their lab publication/s therefore sections 211-215 cannot assure the accuracy of the measurements. It has been mentioned in lines 181-182 that calcite standard were analysed for consistence. Data for this reproducibility will be the best indication of accuracy and reproducibility of the method and has to be reported.

- Section 2.5/2.5.1/2.5.2 (lines 217-239). It is necessary to break this down in sections if there are only 2 sentences in each section?

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