

Interactive comment on “Rapid recovery of Ediacaran oceans in the aftermath of the Marinoan glaciation” by Anthony Dosseto et al.

Anonymous Referee #2

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The manuscript presented reports mainly on lithium isotopes in Ediacaran cap dolostones from South Australia (Nuccaleena Formation) and China (Doushantuo Fm) to investigate changes in ocean chemistry that followed the Marinoan deglaciation. In this review, I will focus on the lithium data since they present, from my point of view, the main weakness of this manuscript and do not merit publication in their current form.

The authors are using a new dissolution technique that has been developed and setup by them and is cited as Taylor et al. (2018). This paper is, however, a manuscript or preprint and since September 2018 under review for the journal *Climate of the Past* and not as yet accepted. In addition, the authors claim that this dissolution or leaching technique is specially set up for dolomites and that only Li from the carbonate/dolomite is leached without any contributions from the siliciclastic detrital component. As such,

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the presented data should represent the elemental and lithium isotope composition of the dolomite. While the leaching technique might work for pure carbonates like corals and dolomites, by looking at the results in Table 2, I doubt that this works for impure dolomites. In addition, there seems to be a big discrepancy between the described leaching technique and the results presented.

The authors report that they leached 1 gram of samples with 20 ml (Taylor et al. 2018) of 0.05M HCl for 1 hour. This should dissolve about 5% of the carbonate and should give a rough Ca concentration in the leachate of about 11000 $\mu\text{g/g}$. The Ca concentration in the leachates is however on average only 256 ppm. Assuming that ppm here is equivalent to $\mu\text{g/g}$, the leachate contained considerably less carbonate, about 0.1% and this doesn't sound right. Admittedly, there are ambiguities associated with the use of 'ppm' but it is not made clear in the manuscript. Alternatively, the authors could have reported the concentration of the 20 ml leachate and this should give 343 mg/L for Ca and 207 mg/L for Mg. In any case, if only material is leached from the dolomite, the Mg/Ca should be around 0.6, but it is instead on average of about 1 and ranges between 0.2 and 1.5. So, something else must have been leached as well. Interestingly, the samples with the lowest Mg/Ca are the ones with the highest amount of calcite (Table 1; note a significant linear correlation between Mg/Ca and the calcite concentration) and the samples with the highest Mg/Ca are the ones with high amounts of the silicate i.e. phyllosilicate minerals (linear correlations between groups of samples and mineral abundances; btw the mineral percentages given in the text line 210 are much higher than what is given in Table 1). That not only dolomite was leached is also obvious from the Al concentration. An average value of 40 ppm looks initially good, but if one assumes that indeed only the dolomite was leached, the Al concentration must have been on average as high as 35000 $\mu\text{g/g}$. If we just focus on the ratio, an Al/Ca of 0.16 as given by the data in Table 2 is massive and cannot be leached out of the dolomite alone, most of the Al must have been leached from the silicate component in the sample. Problem is, leaching considerable amounts of aluminium out of silicates results most certainly in leaching lithium as well. Most lithium studies demonstrate

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low Al concentrations in the solution that gets analysed for Li, but this is not the case here. Initially, the Li concentration also appears low as expected from pure dolomite, but again, if one compares it with the Ca concentration, the Li concentration would be of 28 $\mu\text{g/g}$ on average and this is well above everything you can have in a carbonate; the same applies if one is just comparing the Li/Ca ratio. The lithium concentration in carbonates is usually well below 2 $\mu\text{g/g}$. If we consider a solution of 5% carbonate in 20 ml, we should find only around 5ppb Li and this is again much lower than the reported average of about 33 ppb in Table 2. If the majority of the Li in the analysed leachate is not from the dolomite, the Li isotope composition cannot represent the composition of the dolomites and can, hence, not be used to investigate changes in ocean chemistry that followed the Marinoan deglaciation.

The manuscript does also not convince that the analytical procedure for lithium is robust. There is vital information missing concerning the e.g. yield and how it was assessed, the procedural blank and most importantly there is no information on the accuracy or on the precision of the Li isotope measurements. How did the authors come up with an “external analytical uncertainty” for the Li isotope values of 1.2 ‰ (especially since it is surprisingly big) and what means 2σ . Regarding the yield, in the referenced Taylor et al. (2018) manuscript it is written that “The columns were calibrated with seawater prior to treating the samples to verify that the procedure yielded 100% of the Li”. There are two problems with this. First of all, the seawater data in Table A1 (Column calibration using seawater samples in Taylor et al. (2018)) look not convincing, they scatter between 28.8 and 32.0 ‰. This is a big spread considering that it should be 31.1 ‰ and that seawater has an easy to deal with matrix. Secondly, seawater has a complete different matrix to a carbonate and hence the peak of the Li recovery could be easily shifted. This can only be monitored by taking splits of the solutions collected before and after the column procedure and demonstrating that $<0.1\%$ of Li was present in these splits. I would also suggest to not only refer to the paper from Balter and Vigier (2014) but to give a brief description of the method, or rather a detailed description as long as the Taylor et al. (2018) manuscript is not accepted.

The data screen exercise mentioned above can unfortunately only be done for the Australian samples since no mineral concentrations and only limited i.e. insufficient elemental concentrations are given for the Chinese section (Table 3). To assess the purity of the leachate and the validity of the Li data, one needs to have an idea about Ca, Mg and Al concentration. There is, furthermore, no information on the uncertainty of the element concentration data provided. The authors might argue that the mineral and elemental information for the Chinese section is of no interest since the material is anyhow diagenetically altered, but I do have doubts about the assessment of the diagenetic overprint given in 5.1. Dolomitisation and diagenesis. In general, even if Neoproterozoic carbonate sections are regarded as well-preserved, one still has to visually screen them and this should start already by taking the samples in the field and should be followed by carefully selecting material that does not contain evidence of secondary alteration or recrystallization usually checked by SEM and CL; has this been done before taking the 1 gr of sample? If yes, that should be documented. To further assess the impact of diagenesis on the sections sampled, the authors (line 257) measured oxygen and carbon isotopic compositions on bulk rock samples of both Nuccaleena and Doushantuo Fms. They report a positive relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for the Doushantuo Fm of $R^2 = 0.49$, but not for the Nuccaleena (Figure 4). If I however, replot the data, I get a much lower R^2 and more importantly no statistically significant correlation. Line 265: The effect of diagenesis on Li isotopes was also tested using the Mn/Sr values. I do agree with the authors that an increased Mn/Sr in Neoproterozoic carbonates does not always implies diagenetic alteration, but they forgot to mention in the text that the Mn concentration is unusually high compared to Sr and that the Mn/Sr goes up to 33 (Fig. 5) with only a few samples showing more “normal” ratios. That there is no clear relationship in the leaching solutions between $\delta^7\text{Li}$ values and Mn/Sr (Line 268) is not a robust argument that a diagenetic imprint on Mn/Sr has neither a measureable nor a systematic effect on Li isotope compositions. As such I do not see a good argument why the Chinese section is the one that is diagenetically altered.

In general, the data are poorly visualized. I am missing a proper stratigraphic section with all isotope and lithological data included. There is also loads of interpretation already in the results section.

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