

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

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We would like to thank Referee 2 for the constructive comments. Each enquiry is addressed below in the order they appeared in the review.

From Referee's comment C1 to the penultimate paragraph of comment C3, these comments in essence refer to Taylor et al. (2019). Although we acknowledge the difficult job presented to the referee since at the time Taylor et al. (2019) was not accepted, the comments do not directly refer to the present manuscript. Since, Taylor et al. (2019) has been accepted for publication in Climate of the Past (as of 11 March 2019), and trusting Copernicus' peer-review system we have to consider the results in Taylor et al.

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(2019) as scientifically sound.

Nevertheless, it is possible to provide evidences that support the applicability of the protocol in Taylor et al. (2019) to this study: in our dataset, there is no relationship between  $\delta^7 Li$  and several proxies for silicate contamination in the leaching solution: Li/Ca, Al/Ca or Al/Mg (see Fig .1 for the Nuccaleena Formation). While the absence of evidence is not evidence of absence, and while silicates may be leached with carbonates during sample preparation, if silicates dominated the  $\delta^7 Li$  of the leaching solution (as they would if present in significant amount, since Li is much more concentrated in silicates compared to carbonates), we should observe a relationship between  $\delta^7 Li$  and Li/Ca, Al/Ca or Al/Mg. This is not observed.

Although samples with Li/Ca >  $20x10^{-5}$  also show low  $\delta^7 Li$  values, there is no systematic variation of the Li/Ca ratio with height above the base of the formation (Fig. 1). Thus, the increase in  $\delta^7 Li$  values at the base of the formation is not explained by high Li/Ca (and thus silicate contribution). Even if we rule out samples with Li/Ca >  $20x10^{-5}$ , the conclusions of the study remain: there is a rapid increase in  $\delta^7 Li$  values at the base of the form low modelled  $\delta^7 Li$  values at the end of the Marinoan glaciation to the values observed in samples with Li/Ca <  $20x10^{-5}$ .

In regard to information about quality control of Li isotope data (yield and how it was assessed, procedural blank and accuracy or precision), the yield was assessed during column calibration and it was verified to be 100% (which is critical for accurate Li isotope measurements). Total procedure blanks were routinely measured and yielded 2 ng of Li. This represents a contribution to the Li isotope ratio of samples of 0.03 ‰. Accuracy could only be assessed using seawater (see below), since we do not have access to a carbonate reference material (which would have been ideal). While Bastian et al. (2018) recently provided recommended values for calcium carbonate standards Jcp-1 and Jct-1, these materials are not commercially available anymore (and most labs are unwilling to share their stock, which is limited). However,

measurement of a Holocene *Porites* coral yielded a  $\delta^7 Li$  of 20.6 ‰, which is similar to values reported for modern *Porites* in Marriott et al. (2004) (between 18.4 ± 0.4 and 19.1 ± 0.4 ‰). Measurements on a 204,000yr-old *Favia* coral from Cook Islands also yielded a  $\delta^7 Li$  of 20.5 ± 0.5 ‰(2 SE; n=4). These details can be included to a revised manuscript.

Referee 2: 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  $2\sigma$ .

Our response: The external analytical uncertainty was calculated by processing separate aliquots of the same sample through the entire process (leaching, chromatography, analysis). This was done for several samples. This error is indeed greater than errors reported when replicating samples that undergo total dissolution (for instance, in our lab we obtain a  $2\sigma$  error of 0.2 % for silicate reference material JG-2 which undergoes total dissolution), and may be attributed to the leaching step. Note that 1.2 ‰ is small compared the range of values observed in the dataset (about 10 ‰).  $2\sigma$  refers to 2 standard deviations.

Referee 2: 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.

Our response: Note that:

1. The range of values we report in Taylor et al. (2019) (28.8-32.0 ‰) is similar to that in the literature (28.0-32.5 ‰; Pistiner and Henderson, 2003; Carignan et al., 2007). Furthermore, this is only a 1.3 ‰deviation from the accepted value, which is similar to our external uncertainty (see above) and small compared to

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the range of variation observed in the samples (about 10 %).

 Seawater is actually a more difficult matrix because of the abundance of Na, which is critical to remove for Li isotope measurement: Na/Li is about 100 times greater in seawater than in carbonates (this is also the case for dolostones, e.g. Fritz and Katz, 1972; Land and Hoops, 1973).

## Referee 2: seawater has a complete different matrix to a carbonate and hence the peak of the Li recovery could be easily shifted.

Our response: Since Referee 2's comments were received, we have produced an elution curve using a dissolved coral (i.e. calcium carbonate). The elution curve is similar to that produced using seawater (Fig. 2). There is a small shift in Li elution, however this is accounted for by the chosen Li elution volumes. While it seems Li and Na peaks are closer with a carbonate matrix, as pointed out above, the Na/Li ratio of carbonates is about 100 times lower than that of seawater. Thus, even if a greater proportion of the Na peak was collected with the Li elution for carbonates, this still results in a negligible fraction of Na in the final Li elution (i.e. after two passes on the column). For seawater, after two passes on the column, 0.4-0.6 % of Na remain in the Li elution. The elution curve for carbonates show there's 1.6 % of Na left in the Li elution after two passes. Considering that (i) the Na/Li of carbonates is about 100 times lower than in seawater and (ii) we always load the same amount of Li on the column (about 60 ng), after two column passes the amount of Na left in the Li elution for carbonates would be about 30 times lower than that when processing seawater.

#### Referee 2: give a brief description of the method

Our response: The methods given in the original manuscript are indeed too succint, and more details would be given in a revised manuscript, as those presented above.

Referee 2: 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

Our response: This is indeed correct. Nevertheless, in the original manuscript we discuss that the Chinese section may have been affected by diagenesis (using C and O isotopes) and thus these date are not used in the model presented in the discussion.

Referee 2: no information on the uncertainty of the element concentration data provided.

Our response: precision on element concentration has been assessed by replicating a sample through the whole process (leaching, chromatography and analysis). It is better than 1% for Li, Mg and Ca, 1.5% for Mn and Rb, 6% for Ti and 9% for Al. Error bars are shown accordingly in Fig. 1 (within the symbol size if not shown).

Referee 2: In general, even if Neoproterozoic carbonate sections are regarded as wellpreserved, one still has to visually screen them and this should start already by taking the samples in the field and should be flowed 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

Our response: Samples of the Nuccaleena Fm were taken from the same section in the field as the one sampled by Rose and Maloof (2010), Kunzmann et al. (2013) and Liu et al. (2014). In these studies, they all propose that dolomite is primary and argue against a diagenetic overprint. As indicated in the original manuscript, Hoffmann et al. (2007) indicated that dolomitized carbonates are commonly coarsely recrystallised and occur at the top of shoaling sequences, while the Nuccaleena Fm is fine-grained and was deposited at the base of a transgressive-regressive

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sequence. Since we received the Referees' comments, we have undertaken SEM-EDS analysis on selected samples. They typically show fine-grained dolomite, as observed by authors cited above at the section sampled, and where calcite is detected it is in veins cutting and thus post-dating the dolomite, not the other way around (Fig. 3).

Referee 2: 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  $\delta^{18}O$  and  $\delta^{13}C$  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.

Our response: As Referee 2 points out, this can't be thoroughly tested because we don't have mineralogical data for these samples. Note that if one suggested that the Doushantuo Fm data are also a useful proxy for Neoproterozoic ocean composition (like the Nuccaleena Fm), Li isotope variations in the Doushantuo Fm would show agreement with those in the Nuccaleena Fm, suggesting a global signal. In the original manuscript, we are using caution as not to draw this inference unless entirely confident.

Referee 2: 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  $\delta^7 Li$  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 diagentically altered.

Our response: There is no clear relationship in the leaching solutions between  $\delta^7 Li$ 

values and Mn/Sr, which is a good proxy for diagenesis as Referee 2 acknowledges. Furthermore, there is also no systematic change in  $\delta^7 Li$  for samples that have high concentrations of silicate minerals and high Mn/Sr ratios: some have a low  $\delta^7 Li$ , others a high  $\delta^7 Li$ . Thus, there is no evidence for a systematic effect of (i) diagenesis or (ii) silicate mineral contribution on  $\delta^7 Li$ . It does not imply it is not there, but it is just not significant enough for the range of  $\delta^7 Li$  values we measure (about 10 ‰).

#### Referee 2: the data are poorly visualized.

Our response: This can be fixed as suggested by Referee 1 (merging figures into panels).

# Referee 2: I am missing a proper stratigraphic section with all isotope and lithological data included.

Our response: This can be added, but it is of little value since there is only one lithological unit (stratigraphic sections are more useful when there are several units). If the editor feels this is important, such stratigraphic section can be included to a revised manuscript.

#### Referee 2: There is also loads of interpretation already in the results section.

Our response: This can be easily fixed by being more strict about what should be in the Results section in a revised manuscript.

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Fig. 1.



Fig. 2.

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Fig. 3.