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Interactive comment on “A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations: the key role of climate” by N. Vigier and Y. Godderis

Anonymous Referee #3

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This clearly-written paper from Vigier and Godderis (henceforth V&G) provides a new perspective on the Cenozoic record of seawater Li isotope composition, adding to the growing number of recent papers on this important topic. Although my review of this submission is critical, I am supportive of this effort and think that it has promise to be a valuable contribution to ongoing discussion. This manuscript addresses a topic well suited to this journal, and I intend my comments to be constructive.

The modeling approach of V&G is very similar to that used by Li and West (2014, EPSL; henceforth L&W), with some notable differences. Given their similarities, and my familiarity with the latter paper, part of this review will focus on comparison of the approaches. Both papers use an analogous isotope mass balance (Eqs. 1-3 in V&G)

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and solve for the value of $\delta^{7}\text{Li}_{\text{riv}}$ through time (note L&W call this $\delta^{7}\text{Li}_{\text{diss}}$, a term that is used differently by V&G). While V&G consider one case (one set of parameter values and forcings, with results in their Fig. 3), L&W consider a range of possible scenarios (they focus on the possibility of changing the sinks from seawater with time but also present cases where these are constant, analogous to V&G). The solution presented by V&G (Fig. 3) is similar to Scenario 3A of L&W; both use similar constraints on dissolved $\delta^{7}\text{Li}_{\text{riv}}$ (Eqs. 8-9 in V&G), allowing Li release to be incongruent with respect to primary mineral weathering. V&G prescribe change in release of Li from primary minerals based on assumed changes in solid Earth degassing fluxes of carbon and assumptions about the C cycle (their Section 2.2; see my comment on this below). In contrast, L&W scenario 3A holds the Li release from primary minerals constant. Since the degassing fluxes used by V&G do not change much, the two cases end up being fairly similar. Thus the curves in Fig. 3a of V&G (henceforth their ‘A solution’) are similar (at least in overall trend) to the curves for Scenario 3A in Fig. 4 of L&W. One important difference between the papers is that V&G identify a second possible mathematical solution to the same set of model equations, their ‘B solution’ (presented in Fig. 3b). L&W overlooked this second solution because it lies outside of the parameter ranges they considered. Arguably, this B solution is highly unlikely or even implausible geologically (see comments below). That said, this alternative B solution presented by V&G is real, at least when the problem is set up as they have done, and in that context it is new and relevant.

Although I view the structure of their model as being reasonable and am pleased to see another group working to shed additional light on this topic, I disagree with a number of aspects of the interpretation presented by V&G. They argue in favor of the ‘B solution’ on the basis that it is more “geologically reasonable.” They then use this solution to calculate what they describe as “soil formation rate” through time. Based on the decrease in these inferred soil formation rates, they argue for a climatic control on soil production and continental weathering. My own view is that these arguments are not well supported, particularly in the following aspects:

(1) V&G focus only on their B solution, a choice that I do not think is well justified, for the following reasons:

(i) V&G exclude the A solution (Fig. 3a) on the basis that the required decrease in Li dissolved riverine flux with time is not consistent with geological evidence (Section 3.1). I can see the general case for saying Li fluxes probably did not decrease dramatically since 50 Ma. However, I find it problematic that V&G rule out anything other than their B solution despite only considering one set of parameters and forcings. This is especially the case since some of the parameter values that V&G use appear relatively ad hoc and differ from previous work (such as those used in Misra & Froelich's 2012 Science paper) without clear rationale (e.g., 14‰ fractionation during reverse weathering, rather than 16‰ a relatively low fractionation during weathering, and a low hydrothermal flux). The use of different values does make a difference to the results. Moreover, the change in hydrothermal degassing of C over time, which is critical to the V&G model solution, is not well constrained (e.g., consider recent alternative degassing reconstructions from Lee et al., 2012, Geosphere and van der Meer et al., 2014, PNAS). Considering other combinations of parameters and forcings that are consistent with geological evidence leads to possible solutions that do not require either large decreases in Li dissolved riverine fluxes towards the present day (as in V&G Fig. 3a) or large increases (as in V&G Fig. 3b). Several of these other solutions are shown in Fig. 4 of L&W. V&G acknowledge in their Introduction that they are not embarking on an exhaustive study of different parameters, since their purpose is to show that there is a (previously unrecognized) solution that does not require large changes in $\delta^{7}\text{Li}_{\text{riv}}$. This is a reasonable thing to do, and their results demonstrate this solution exists. But showing that this additional solution is possible is not alone a valid justification for throwing out the whole family of other solutions that include some which do not require large changes in flux. Nor do I think that it provides adequate grounds for arguing that “the Li isotope composition of rivers plays only a minor role in the ocean isotope variation” – yes, that is true for the one case shown in Fig. 3b, but it is not true more generally. V&G may be right that continental dissolved Li fluxes did

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not decrease greatly since 55 Ma. But nor does the Li isotope record mean that these fluxes had to increase, as assumed by V&G in their Discussion.

(ii) Although the B solution of V&G is mathematically viable, I estimate that it would imply trapping of $\sim 99\%$ or more of the Li released by primary minerals in secondary phases at 50-60 Ma. V&G haven't reported their model results in a table in this version of the manuscript, but looking at their graphs, at ~ 55 Ma, $F_{\text{friv}} < 1 \times 10^9$ mols/yr, and $F_{\text{sp}} > 80 \times 10^9$ mols/yr, requiring that $>80/81$ of the total Li initially released ($F_{\text{sp}} + F_{\text{friv}}$) is trapped in secondary phases, SP. I don't dispute that some Li is of course trapped in clays and not released congruently. But I am not aware of weathering settings on the present-day Earth characterized by nearly complete Li retention (the simplest evidence being the observed substantial dissolved Li fluxes in rivers, unlike for elements such as Al, Ti, or Zr, which are retained at 99% or higher). Although the world at 55 Ma was probably very different from today, it seems a stretch to suggest that the total global dissolved flux was characterized by processes that are totally different from any region on the present-day Earth.

Here is another way to look at this: V&G argue the ~ 23 ppm Li in kaolinite could allow for significant Li retention in laterites. Yes, but 99% retention would mean Li was effectively immobile, and so Li should track an element like Al. Instead, the Li/Al (g/g) ratio in kaolinite is $\sim 1.1 \times 10^{-4}$ (for 21 wt% Al in kaolinite, and the 23 ppm Li suggested by V&G) while the continental crust is $\sim 2.6 \times 10^{-4}$ (8.1 wt% Al and 21 ppm Li, from Rudnick & Gao). These aren't intended to be precise but illustrate that even the high concentrations of Li in kaolinite require significant leaching relative to bulk rock (to explain the lower Li/Al ratios). The nearly complete retention required by Fig. 3b at 55 Ma does not seem to me to be consistent with these observations.

I think it is also relevant to point out that the elegant analytical solution provided by V&G has some instability. I was able to basically reproduce their results, but if the seawater isotope record is averaged at a smaller time step (e.g., 1 Ma rather than 5 Ma as used by V&G), then their model parameters lead to complex solutions to the quadratic

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equations. This is because the model equations (for the V&G choice of parameters) did not (at least in my attempt to solve them) have real solutions above a certain seawater value, which for me worked out around 30.45‰ a value that is lower than some of the actual observations of seawater composition at times in the recent past (i.e. within the last 5 Ma, including, ironically, present day observations at 31‰). It would be nice if the analytical solution could be shown to work for the present day.

In summary, I think V&G succeed in showing (e.g., in Fig. 3b) that seawater Li isotope mass balance does not absolutely require a change in $\delta^{7}\text{Li}_{\text{riv}}$ as an inherent characteristic of the solution to the set of mass balance equations. But with the above points in mind, I personally see little justification for making the further case that large increases in Li flux (Fig. 3b) provide the most “geologically reasonable” explanation for the seawater record, as argued by V&G and used as the basis for the the wider conclusions in Section 3 of their paper.

(2) Even if Fig. 3b is taken as the most reasonable explanation for the oceanic Li isotope record, I find the many of V&G’s further interpretations to be problematic from my perspective. V&G use the flux of Li going into secondary phases (F_{sp} ; Fig. 4) to calculate a “soil formation rate” by multiplying Li concentration in clays times F_{sp} . One problem here is the assumption of constant Li concentration in secondary phases over time. They acknowledge this is a potential limitation. Assuming Li concentration does not vary, as V&G propose, the more critical problem is that V&G are calculating a rate of secondary phase formation, which is not the same as soil formation. Reviewer #1 has also alluded to this issue. Formation of soils and formation of secondary phases may be very different, since soil also includes primary minerals (and organic material), in varying proportion. This definition is important for several reasons. It complicates any comparison with the global denudation rates from Syvitski (end of Section 3.1); the global denudation flux is definitely not all secondary phases, nor is it fixed to have the same proportion of secondary phases over time. It also questions V&G’s argument that Fig. 5 shows “a major role for climate on continental weathering.” Fig. 5a shows

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a change in the amount of secondary phase formation (or perhaps the amount of Li in secondary phases), not a rate of soil formation, nor a change in global continental weathering.

This latter point relates to what I see as an important additional shortcoming in the logic of Section 3.2. V&G have already prescribed the rate of global chemical weathering, when they use the flux of Ca and Mg released from primary minerals to drive their model. I find it logically inconsistent to then use the model results to infer how global weathering has changed!

As I see it, V&G might be able to speculate about changes in the ratio of secondary phase formation relative to primary mineral weathering. Assuming that their result is viewed as robust, I can see making the case that Fig. 5a implies that the ratio of secondary phase formation:primary mineral weathering decreased since 55 Ma. Then there is the question of why, and what this means in terms of the global weathering system. I think addressing these questions requires real care in the interpretation of the relationship with the O-isotope curve. A decrease in the ratio of secondary phase formation to primary mineral weathering could be related to a cooling climate. It could also be consistent with a shift in global denudation regime, or perhaps to a change in biological or hydrologic roles in secondary phase formation. I am not sure how these possibilities can be rigorously distinguished and don't really see how Fig. 5 provides "good evidence of the predominance of climate over mechanical erosion," as V&G argue. I think the classic problem of 'correlation vs. causation' needs particularly careful attention in the analysis here. Indeed the coincidence of secondary mineral formation and O-isotope curves might indicate that one is driving the other (climate change represented by the O-isotopes driving the change in secondary mineral formation). Or, these curves might follow the same trend because they are both driven by the something else (e.g., both driven by changes in the global weathering regime) and thus not directly causally related. . .

The following are some more specific comments:

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Although I think it is quite a clever idea to try to use the C cycle mass balance to help constrain the global Li isotope mass balance model, it involves some critical assumptions not explored by V&G. The requirement of mass balance in the C cycle is actually that $FCO_2, sources = FCO_2, sinks$. This is subtly but importantly different from V&G eqn. 4, where they implicitly assume that hydrothermal degassing is the only source, and that alkalinity from silicate weathering is the only sink. As V&G are undoubtedly aware, there are several other sources and sinks, such as those associated with metamorphic degassing and the organic C cycle, that may have changed significantly over the last 60 Ma. Inclusion of these terms in eqn. 4 would, of course, complicate solution of their model. On the other hand, not including them in eqn. 4 means that the V&G model solution at best represents one possible scenario, rather than reflecting a single well-constrained solution for the coupled Li and C cycles, as they seem to imply. This is all the more the case since past changes in FCO_2, hyd are highly uncertain and much debated (as noted above).

I also find it somewhat inaccurate for the authors to describe their use of the C cycle mass balance constraint as the “Walker thermostat,” because the Walker et al., 1981 paper focused on the need for a feedback between temperature and the climate system, which they proposed could be through a climate-dependence of the weathering sink in the C cycle. This isn’t exactly the same as demanding mass balance in the C cycle, which is the constraint that V&G are using in their model.

In Section 3.1, V&G argue that dissolved continental fluxes of Li probably did not decrease since 55 Ma. I tend to agree that this is probably the case, but I am not sure the logic as set out by V&G is totally robust. The first reason that V&G cite is the record of other elements and isotopes in seawater, notably Sr and Os – but they have already established that Li is likely to be decoupled from the fluxes of soluble elements such as Ca and Mg, and so presumably also Sr and Os. So it seems somewhat inconsistent to try to use these records to argue for any given change in the flux of Li. The second reason that V&G cite is the high Li concentration in laterites. But were there more

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laterites at 55 Ma? This does seem plausible, but it would be nice to see some clear evidence, carefully presented by the authors – and surely it is circular to use the model results (i.e. as presented in Section 3) as that evidence.

The value for C/Li_{hyd} reported in Table 2 (6.67×10^{-4}) cannot be correct – this would imply more Li than C coming from hydrothermal systems! Perhaps the reported value is Li_{hyd}/C , so $1/k^2$? Even then, it is not clear how the authors calculated this value. This needs to be more clearly explained in the paper, with some more clear justification for the logic.

It would be nice if the authors included tables, either in the main text of the supplement, with their model inputs (e.g., the averaged values they use for seawater Li) and their results. I think it reasonable to expect these results in table form in addition to the figures.

I think the authors could do a better overall job of putting this paper in the context of other recent work on the Li isotope record. The paper by Li & West (2014, EPSL), which I have discussed in detail above because of the similarity of the model structure to that used by V&G, is one example that also highlights how the ocean sink might additionally modulate seawater isotope composition (something not mentioned by V&G). But I also think it would be important for V&G to consider two other recent papers on this topic: one by Wanner et al. (2014, Chemical Geology; mentioned by one other reviewer), and the other by Froelich and Misra (2014, Oceanography). Since these both deal with interpretations of the Cenozoic Li isotope curve, I think it is reasonable to expect at least some discussion of them, and for the current work to be put in that context.

V&G do not address the highly variability in Li concentration in different rock types (e.g., an order of magnitude lower in basalt than in granite), which could very significantly affect eqn. 6, especially if proportions of weathering of different rock types changed over the Cenozoic. I anticipate that the model results might be quite sensitive to such changes if variable Li concentration were taken into account.

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