Answer to C. Wanner (Referee 1)

General comments

N. Vigier and Y. Godderis present a new approach for simulating the Cenozoic seawater Li isotopic record. I believe that the manuscript will form an important contribution to help improve the understanding of the previously published seawater δ7Li record (Misra and Froelich, 2012). Most importantly it does not rely on geochemically unlikely congruent weathering to explain the low seawater δ7Li value observed at the Paleocene-Eocene boundary. Moreover, the authors focus on climate as a potential driver for explaining the change in seawater δ7Li, which to my knowledge is a novel interpretation. The presented simulations are well documented and based on mostly sound assumptions. The manuscript also benefits from a clear structure and a fluent language.

We thank Christoph Wanner for this positive comment and his helpful remarks below that will be taken into account into the revised manuscript.

Nevertheless, I have two main points for improvement:

1. Two studies dealing with exactly the same topic have been published since the submission of the manuscript. These are:

Li, G., West, J. A. 2014. Evolution of Cenozoic seawater lithium isotopes: Coupling of global denudation regime and shifting seawater sinks. Earth and Planetary Science Letters 401, 284-293.

Wanner, C., Sonnenthal, E., Liu, X-M. 2014. Seawater δ7Li: A direct proxy for global CO2 consumption by continental silicate weathering? Chemical Geology 381, 154-167.

I suggest relating the main findings of these new studies to the simulations results presented in the submitted manuscript. This is important, because both published studies conclude that tectonic uplift and not climate is the main driver for the Cenozoic seawater δ7Li increase.

We will cite these two references in the revised manuscript, and will compare our results with them (see also *Answer to Reviewer 3* below). Please note that one of them was not available at the time of the submission of our manuscript and the second only a few weeks before. We apologize for this.

2. While I mostly understand and agree how the Cenozoic riverine Li flux and corresponding Li isotopic composition were simulated I do not fully understand how the parameter FLisp corresponds to the soil formation rate on the continents (see specific comments later on). Clarifying this relationship is important because the entire discussion regarding the control of climate on seawater δ7Li is based on this relationship.

We will clarify this point in the text. We agree that FLisp strictly leads to secondary phase formation rate, by using Li concentrations in these phases. However, we consider first that most secondary phase are formed within soil profiles at the continental scale, and even if some have the time to be formed during the river transport, this fraction is likely minor compared to the formation of thick soils and kaolinite-rich laterite. Second, riverine dissolved Li concentrations are often lower than the saturated soil solutions or aquifer waters; As a consequence, any secondary phase formed during river transport should incorporate minor quantities of lithium.

Specific comments

Page 3031, lines 17-19, absolute value of fractionation factor, -10 and -25 ‰: It is a little bit confusing to first talk about absolute values and then using a minus sign when listing

published fractionation factors. As far as I understood, fractionation factor were used as positive values in any of your equations. Is this correct?
Yes, we will be more consistent in the text about the way we present isotope fractionation factors.

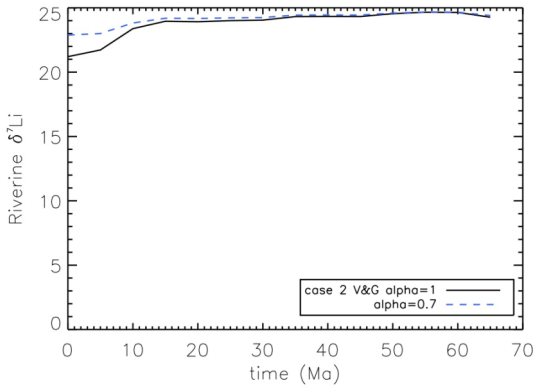
Page 3034, equation 6
What is the exact meaning of FLidiss? It is stated that it refers to the "flux of Li released into continental waters during the dissolution of continental rocks". Accordingly, I suspect that this parameter reflects primary silicate dissolution and does not take into account secondary mineral precipitation. Is this correct? The reason why I am asking is that, in my opinion, the amount of CO2 consumed by silicate weathering depends on the amount of primary silicate dissolution as well as the amount of secondary mineral precipitation and not only on the amount of primary silicate dissolution. Secondary mineral precipitation is important because it forms a proton source that needs to be subtracted from the amount of primary silicate dissolution (i.e., proton sink), to calculate the amount of CO2 consumption by silicate weathering. An example for such a calculation is given in equation (11) of Wanner et al. (2014).To make the long story short, I think that, if FLi diss refers to the Li flux associated with primary silicate dissolution only, the first part of equation (6) should read something like FCO2riv=1/k x (FLidiss – FLisp).
Strictly speaking, silicate dissolution consumes atmospheric CO_2 by the release of base cations on continental waters (Na^+, Ca^{2+}, Mg^{2+}, K^+). In the absence of sulfuric or nitric acid, the charge of those cations is balanced by the negative charge of dissolved HCO_3^-. Furthermore, at the geological timescale, only Ca^{2+} and Mg^{2+} matter, because neither sodium nor potassium carbonates can precipitate in the ocean. Mg^{2+} is less critical for the Cenozoic times as dolomite accumulation are sparse for this geological period. So the only way for secondary phases to limit the CO_2 consumption by fresh silicate rock dissolution is to incorporate cations, mainly Ca^{2+}. Kaolinite do not contain base cations. Consequently, it does not limit the CO_2 consumption by primary mineral dissolution. Among the common secondary phases able to store calcium, smectites can potentially play a role. Ca-montmorillonite, a common phase "rich" in calcium, contains only 4 Ca^{2+} for 100 Si. This ratio is much higher for primary silicate minerals (50/100 for anorthite, 50/100 for diopside, 11/100 for andesine), solid solutions (33/100 for bytownite, 25/100 for labradorite) and silicate glasses (such as basaltic glass, 23/100). Those numbers translate the mobility of calcium (and magnesium) in the low temperature weathering environment. Most of the calcium released by silicate rock dissolution reaches the ocean in dissolved phase, and thus participate to the CO_2 consumption. This is why we assume that the CO_2 consumption is proportional to the Li flux released by primary dissolution.

But we acknowledge that this means that no calcium is stored in secondary phase. This is a first order approximation. We will clarify this in the revised manuscript. FYI the model can account for storage of cations in secondary phases. In that case, equation 6 can be rewritten as follows:

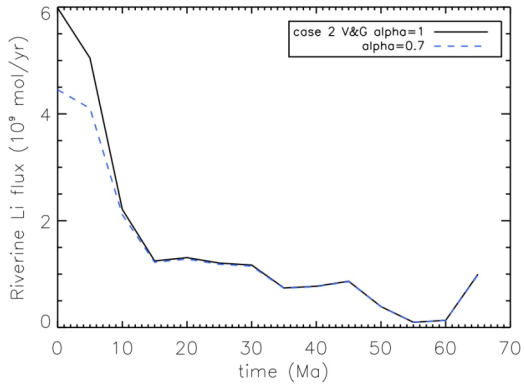
$$F^{CO2}_{riv} = \text{alpha } F^{CO2}_{diss} = \text{alpha}/k_1 \, F^{Li}_{diss}$$

The alpha factor (0<alpha<1) sets the proportion of calcium released by the rock dissolution and transported in the river. In the paper, we set alpha to 1. But the reviewer is right, it can be lower than 1. Owing to the mobility of calcium, values close to 0 are not realistic. The two following plots compare the model results for a value of alpha of 1 (case 2 in the submitted

version) to a simulation where alpha is set to 0.7. The model is weakly sensitive to this parameter.



Calculated time evolution of the Li isotopic composition of rivers (alpha=1 and alpha=0.7)



Calculated time evolution of the riverine Li flux to the ocean (alpha=1 and alpha=0.7)

Page 3035, lines 3-4, soil formation rate

This sentence infers that the variable FLi sp corresponds to the soil formation rate. Because this is a very fundamental assumption for the calculation and discussion that follows later on (Figs. 4-5, pages 3038-3039) I would like to see some explanation why this assumption can be made. According to the definition of FLi sp (page 3034, lines 15-16) this parameter refers to the Li flux into secondary mineral phases. However, if Li isotopic fractionation is also occurring in rivers (e.g., by alteration of the suspended load) such as concluded by Wanner et al (2014) not all of the formed secondary phases and thus not the entire FLi sp contribute to soil formation. This means that there might be a Li flux into secondary minerals that is not participating in soil formation.

Indeed, this parameter reflects strictly a secondary phase formation rate (see also our answer to this point above). Due to crystallization kinetics, the fraction of secondary phase formed during the river transport is likely to be minor compared to those formed in soil profiles or laterites. We will specify in the text that the assumption behind the calculation of soil formation rate is that most Li-rich secondary phases occur in soils (see also our next answer concerning the comparison with the Wanner et al. model).

Page 3035, lines 9-11, "when soil production and thickness increased in the past, we expect that the δ7Li of river waters increased" This statement is in contradiction to Wanner et al., (2014) who presented reactive transport model simulations showing that riverine δ7Li is inversely correlated with saprolite thickness (i.e., low riverine δ7Li at large saprolite thickness). I was thus wondering whether this expectation/assumption is reflected in equation (9) and if yes, how it is justified.

Yes, this assumption comes from equation (9): since clays are enriched in ^{6}Li, more clays formed lead to more ^{6}Li depletion into waters, resulting in higher δ^{7}Li values.

Wanner and co-authors used a complex reactive transport model to simulate the Li isotopic composition and content of continental waters. An important feature of their model is its ability to simulate the weathering reactions inside a weathering profile (e.g. the re-dissolution of secondary phases). Their simulations of the warm Eocene weathering system start from a prescribed thick regolith which already contains altered material, above a fresh granite. Their model is quite efficient since it is well known than thick regoliths are continuously evolving with time, as reflected by the difficulty of dating such profiles (Nahon, 2003). Conversely, our

model cannot simulate such weathering processes, because it is based on budget equations and not on fine scale processes. However, our budget equations require a massive transformation of fresh rocks into regolith during the warm Eocene, which is evidenced in many parts of the world (Beauvais and Chardon, 2013; Retallack, 2008; Tabor and Yapp, 2005; Robert and Kennett, 1992).
So the Wanner et al. model can simulate finely the time evolution of an already existing regolith profile and its impact on the riverine Li content and isotopic composition. The inverse relationship between regolith thickness and riverine δ^7Li arises from a longer residence time of water in contact with depleted secondary phases if regoliths are thicker. This may decrease riverine δ^7Li. In our budget model, the formation of secondary phases from fresh bedrock produce an increase of river isotopic composition, because ^{6}Li is stored in the regolith.
Future studies should merge both methods such that transformation of the fresh bedrock into regolith can be accounted for (our paper), as well as the reactivity of the regolith himself (Wanner et al.).
This will be clearly mentioned in the revised version.

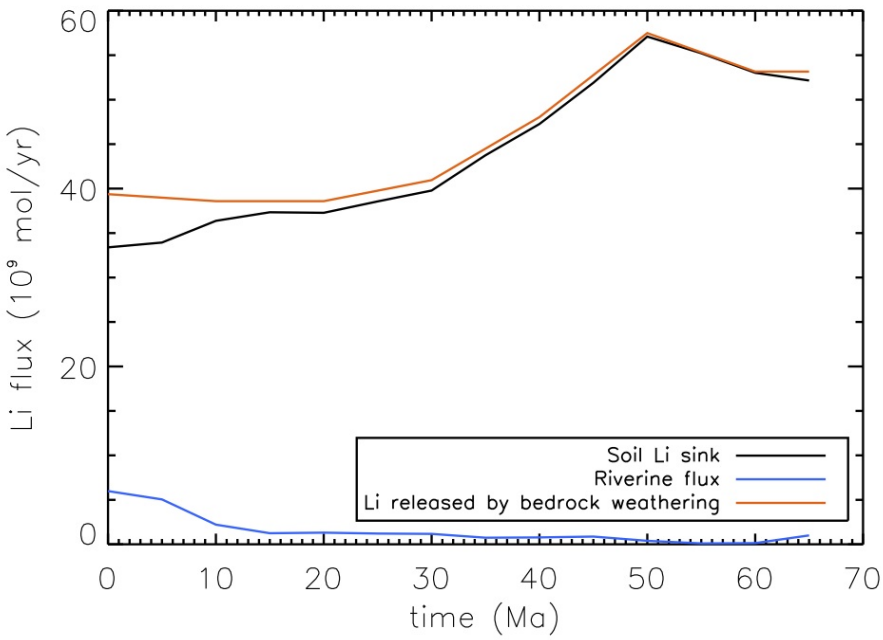
Page 3035, equation 8 The parameter FLi soil is not properly defined. I believe it corresponds to FLi sp and thus suggest using FLi sp instead.
This will be corrected

Page 3035, line 16, average δ7Li value
I believe that 1.7‰ is the value reported for the average continental crust (Tenget al., 2009). In contrast, a value of 0±2‰ was reported for the upper continental crust (Teng et al., 2004).
The value of 1.7‰ represents the average values for different types of granites analyzed by Teng et al., 2009, and is likely to be more representative of unweathered continental silicate material than loess and shales data given in Teng et al., 2004. Given the large uncertainties on both numbers, both estimations are not significantly different.

Page 3037, lines 16ff, discussion of second scenario (Fig. 3b)
I fully agree that the riverine Li flux likely increased during the Cenozoic. It is consistent with our own reactive transport model simulations (Wanner et al., 2014) as well as with the flux and mass balance calculations performed by Li and West (2014). However, I would like to see a discussion about the differences between your results and with the ones of Li and West (2014). In particular, Li and West (2014) concluded that a change in riverine δ7Li is necessary to explain the seawater δ7Li record, whereas you state that a change in riverine δ7Li is not required. I suspect that the different constraint on the riverine Li flux might have caused the different conclusions. While in your simulations the Li flux is entirely free to evolve, Li and West (2014) tied it to the Cenozoic silicate weathering increase such as simulated by Li and Elderfield (2013). A comparison is also important because the different assumptions yielded a large difference with respect to the magnitude of the riverine Li flux increase (factor 2 in case of Li and West, and up to a factor ≈10-20 for your simulation).
We note positively that the reviewer is convinced by our result. Please see our *Answer to reviewer 3* for more details about this aspect and comparison with the Li & West (2014) model.

Page 3037, lines 19-21. "As illustrated in Fig. 4, … due to the decrease of Li storage in soils"
This argumentation would be easier to follow if FLi diss was plotted in Fig.4 in addition to FLi sp. By doing so, it should become clear that FLidiss (and thus weathering rates) did not

change significantly over the Cenozoic, which I think is important to follow the conclusion that climate and not weathering forms the main driver for the seawater δ7Li record.
Here is the requested plot. We also include the riverine flux.



Main Li fluxes. Case B from V&G.

The total release of Li by the dissolution of fresh rocks equals the sum of the flux to the ocean and the sink into clay minerals inside weathering profiles. At present day, the model predicts that about 80% of the Li released by weathering reactions is trapped in clay minerals, a number in agreement with the observation that today, more than 80% of the Li reach the ocean as a particulate flux (calculation based on discharge and fluxes published by Gaillardet et al., 1999 and published average Li concentration for river water and suspended particles, Huh et al., 1998; 2001; Kisakurek et al., 2005; Millot et al., 2010; Dellinger et al., 2014). The weathering release of Li is high during the Eocene because the soil formation is high. This is in agreement with the fact that a wetter and warmer climate resulted in an intense weathering during the Eocene. This intense weathering leads to worldwide production of thick lateritic profiles (Beauvais and Chardon, 2013; Retallack, 2008; Tabor and Yapp, 2005; Robert and Kennett, 1992) (see *Answer to reviewer 3* for more details). An important soil production requires important weathering rates. Furthermore, our Li budget is coupled to the global carbon budget. As a consequence, the CO_2 consumption by weathering balances the prescribed CO_2 degassing (Walker et al., 1981). As a degassing rate, we choose the reconstruction from Engebretson (1992). It is not the most recent one, but it is the degassing history in best agreement with the Cenozoic climate history (reconstructed using a coupled 3D climate-carbon model, Lefebvre et al., 2013).

Technical comments
All suggested corrections will be carefully made in the revised manuscript

Answer to P. Tomascak (Referee 2)

We thank Paul Tomascak for his very positive review.

Answer to Referee 3

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.

We thank the reviewer for this positive introduction and his constructive remarks below.

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) and solve for the value of δ7Li_riv through time (note L&W call this δ7Li_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 δ7Li_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.

An important point is that the paper by Li and West (2014, EPSL) has been available on line on the 28th June while we submitted our manuscript on the 9th June. This makes our paper and the Li and West paper two independent contributions. Anyway, we will of course refer to the contribution of L&W in the revised version.

A preliminary remark: there is an ongoing debate about the main controlling factors of continental weathering, particularly over the Cenozoic. The critical zone community may appear divided into two factions. The first one is supporting the idea that weathering is driven by climate, following the classical feedback loop of Walker et al. (1981). A bunch of papers over the last 25 years are supporting this idea. The other faction is supporting the idea that physical erosion is driving weathering, and hence the numerous orogenies of the Cenozoic are responsible for the global cooling. And there is also a bunch of papers supporting this idea. From the modeler point of view, the reality is probably a mixing of both. Goddéris and François, 1996; Kump and Arthur, 1997 were the first to discuss the complex interaction between weatherability, climate and physical erosion.

We would like also to mention that the reviewer disagrees with our interpretation of the seawater Li isotopic composition, but finally acknowledge that an important feature of our interpretation "might be plausible", a more intense formation of thick weathering profiles at the beginning of the Cenozoic than today.

This in mind, most of the points of the reviewer are related to a comparison between our contribution and the L&W contribution. The L&W contribution belongs more to the erosive faction (although they include other processes as well), while ours is more on the climate side. The problem is that both contributions are using the same dataset, and this is probably the origin of the critical posture of the reviewer: the same data lead to different interpretations. Reconciling the two points of view will not be solved within one paper. But the discussion is constructive. Indeed, things are subtler than it first looks. We show that both solutions are possible. And even if we argue more for one solution, our central aim is to show that there are two, and not only one, Cenozoic lithium stories.

There are much more differences between the two methods than suggested by the reviewer. Of course, the isotopic balance is the same, this equation being a standard equation. All models on Earth are using it. But our model couples the carbon and lithium cycle inside the same set of equations. As such, our model is fully self-consistent. In L&W, continental weathering is taken from another model (Li & Elderfield, 2013) and translated in terms of Li. This may introduce inconsistencies. For instance the hydrothermal forcing is different in both models (fig 5b in L&E, and fig S3 in L&W). Furthermore, the L&W model is designed to test the role of the removal of Li from the seafloor. By doing so, they use simple kinetic laws representing the processes at play. Given what is known about the kinetics of the Li removal during the formation of marine authigenic clays, there is a risk of introducing uncertainties. In our model, everything is based on budget equations and proportionality hypotheses. We are not arguing that our method is better, but the two methods are different.

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:

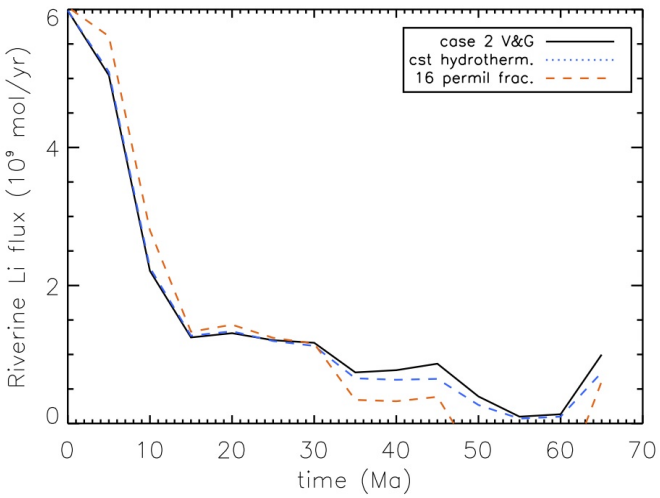
(1) V&G focus only on their B solution, a choice that I do not think is well justified, for the following reasons:
(i) V&G exclude the A solution (Fig. 3a) on the basis that the required decrease in Li dissolved riverine flux with time is not consistent with geological evidence (Sec- tion 3.1). I can 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 δ7Li_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 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.

First, our aim is neither to exclude definitely the A solution, nor to state that scenario B is the only solution. We focus on the B solution because it is the new one.

Second, the degassing rate of the Earth is a big unknown. There are about 8 different reconstructions and they all completely disagree over the Cenozoic (Gaffin, 1987; Engebretson, 1992 (the one used by the well-known GEOCARB model); Larson, 1991; Rowley, 2002; Cogné and Humler, 2006, Vandermeer et al., 2014). Lefebvre et al., 2013, EPSL, demonstrate that the curve proposed by Engebretson (1992) was the only one able to reproduce the climatic evolution of the Cenozoic, and more specifically the CO_2 threshold for the onset of the Antarctic and Arctic glaciations. This is the reason why we choose to use it. Anyway, the solution B is weakly dependent on the shape of the degassing rate, as illustrated below for a run at constant degassing rate (see figure).

Third, the solution B is weakly dependent on the adopted value for the reverse weathering fractionation, 14 or 16 ‰, except that we found no solutions for case B between 60 and 50 Ma. As discussed below, this is related to the very low values displayed by the seawater Li isotopic composition for this time interval. Please also note that the Li isotope fractionation is strongly dependent on temperature. As discussed in Vigier et al. (2008), there is no precise knowledge of the mean temperature at which marine clays are formed at the global scale. Our modeling implies that the corresponding Li isotope fractionation factor is close to 14‰. This is not explored in the present manuscript, but it implies that marine Li-rich clays are preferentially formed in the ocean under rather warm conditions, either close to the middle ocean ridges or at depth. This is fully consistent with our knowledge of Li behavior during clay formation since Li substitute more efficiently to octahedral Mg at higher temperature (Vigier et al., 2008; Decarreau et al., 2012) (adsorption being a minor process).



Time evolution of the riverine Li delivery to the ocean. The black curve stands for case B of our paper. In blue, a simulation assuming a constant hydrothermal flux. In red, a simulation where the Li isotopic fractionation during reverse weathering has been increased from 14 to 16 permil.

Fourth, the 12 scenarii of L&W (fig 4 in their article) are not testing the sensitivity to the parameters, but the sensitivity to chosen kinetics. This means that for a given set of parameters which are fixed, including the isotopic fractionations, they perform valuable tests to the mathematical formulations of several fluxes, such as the role of marine authigenic clay formation. As stated above, our model escapes this problem as it is based only on budgets and proportionality equations.

Fifth, arguing that a solution can be ruled out because it occurs seldom is a wrong argument. A mathematical solution exists or does not exist. The question is then the geological interpretation.

We would like also to point at another difference between our model and L&W. It is meaningless to directly compare our model output with L&W. L&W are testing processes that are not included in our model, in particular the removal of oceanic Li by various processes. Conversely, by writing simple budget equations and assuming the proportionality between carbon and lithium fluxes, we found two solutions, one of them being unreachable with the model of L&W because the way the models are written is different. Any coincidence between our B case and some simulations of L&W is fortuitous.

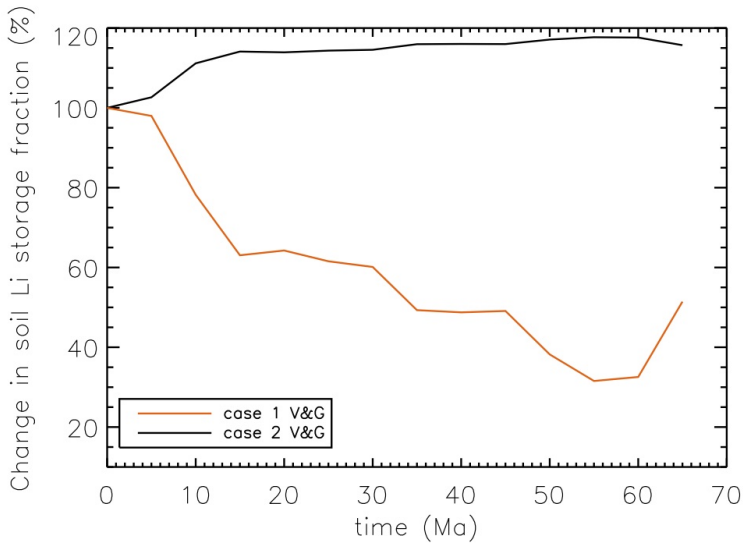
(ii) Although the B solution of V&G is mathematically viable, I estimate that it would imply trapping of ~99% or more of the Li released by primary minerals in secondary phases at 50-60 Ma. V&G haven't reported their model results in a table in this version of the manuscript, but looking at their graphs, at ~55 Ma, Friv < 1 x 10ˆ9 mols/yr, and Fsp > 80 x 10ˆ9 mols/yr, requiring that >80/81 of the total Li initially released (Fsp+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.

Two points here : today, about 85% of the riverine Li reach the ocean trapped in particulate phase (based on published data for river fluxes and associated Li concentrations, see also *answer to reviewer 1*). Rising to 99% is not such a big increase. When criticizing one scenario, it is important to check what the other is doing. The figure below shows the change in Li storage in weathering profiles over the Cenozoic, relative to the present day value. Scenario A requires a dramatic change over the Cenozoic, with a 3-fold increase in Li storage from 55 to 0 Ma. This requires a major change in the global weathering regime. Conversely, case B requires only a 15 % decrease of this storage over the Cenozoic, and thus no big change in the global weathering regime.

Nevertheless, we agree that 100% storage of the Li released by primary mineral dissolution may be excessive. This high storage occurs at 55 Ma, at a time where the Li isotopic composition of seawater reaches a minima. It does not last so long, but this extreme period will be mentioned in the revised version.

From 60 to 50 Ma, the storage is almost equal to 100 % in the case B. We do not have enough data to infer the global weathering history of the Cenozoic. But this corresponds precisely to the longest and one of the most intense weathering events of the Cenozoic in western Africa (Beauvais and Chardon, 2013, G3). Conversely, case A predicts that only 20% of Li is retained during this event. Given that kaolinites do contain Li with the same abundance than smectite, why should the storage minimal at that time ? However, we acknowledge that 100 % is probably extreme, but the important things here are the general trends of both solution. This will be emphasized in the revised version. Note also that new soil Li data recently published by Ryu,

Vigier et al (GCA, in press) confirm that Li is as immobile as Nb (the most immobile element of all the studied profiles) in kaolinite rich soils.



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 ~1.1 x 10ˆ-4 (for 21 wt% Al in kaolinite, and the 23 ppm Li suggested by V&G) while the continental crust is ~2.6 x 10ˆ-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.

Al is certainly not an immobile element in weathering profiles. Please see above our answer related to the Li mobility.

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 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.

As mentioned in the text, the residence time of Li in the ocean is 1 million years. This means that the steady-state hypothesis for the isotopic budget is only valid for a timescale of several million years (at least three times the residence time). This is why we choose to smooth the curve on a 5Myr-window basis, to be sure that steady-state can be applied. This is not at all an esthetical choice. Below such a time window, the steady-state hypothesis is not more verified and the time derivative term in the isotopic budget becomes too large to assume it equal to zero. The model becomes simply wrong. The model is not able to simulate short term changes. We will clarify this in the text.
So contrary to what is ironically stating the reviewer, the model works for the present day, given that the present day is taken as the average of the last 2.5 Myr (there is a little boundary effect in

the simulation, unavoidable since no data exists for the future 2.5 Myr).

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 δ7Li_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.

We think that we demonstrate point by point that the case B solution is at least as valid as the case A. We will temper the discussion in the revised version, the most important thing being the existence of two solutions, which cannot be withdrawn so easily.

(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.

We find here the heart of the debate (see our introductory note). It is, at least partly, a question of perspective (erosive vs climatic side)

V&G use the flux of Li going into secondary phases (Fsp; Fig. 4) to calculate a "soil formation rate" by multiplying Li concentration in clays times Fsp. 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. One of the other reviewers 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 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.

It is important to note that Li & West as well as Misra & Froelich reconstructed the Cenozoic Li cycle from the seawater Li isotopic composition, without comparing their model output to any independent data set. We are the first to try this.
As stated in the paper, our goal is simply to check whether the predicted secondary phase accumulation flux is realistic, and of the same order of magnitude as other estimations for erosion fluxes, in particular the famous erosion flux from Syvitsky (line 10, p 3038). As it is the case, our results make sense. Of course soil is more than secondary phases, and we acknowledge the wrong use of "soil formation" on line 13, p3038. We thank the reviewer for noting this, and it will be corrected in the revised version. Note however that laterites, where the largely dominant clay phase is kaolinite, covers 30% of the continental surfaces. But owing to their thickness, they constitute about 85% of the global continental pedogenic cover (Nahon, 2003, Compte-Rendus Geoscience, 335, 1109-1119). We will be more precise about this in the text.

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 something else (e.g., both driven by changes in the global weathering regime) and thus not directly causally related...

This is an important point and the reviewer is undoubtedly aware that all models inverting isotopic data cannot explicitly solve the chicken or egg question. This is the case of the Li and Elderfield (2013), Misra & Froelich (2012), Li & West (2014), and V&G models. Those models are reconstructing the fluxes required to reproduce the isotopic history of seawater. None of those models can predict why these fluxes have changed, because they are not process-based models. So the rigorous methodology that we apply is (1) to concentrate on the new scenarios, the case A being largely discussed in Misra and Froelich (2012; 2014) and in L&W (2014), and (2) to interpret our results in the light of geology. So the direct causality cannot be proven neither for case A (it could be also a vegetation change that produces a gradual change towards a less congruent weathering, instead of mountain ranges as argued in L&W, who knows ?), and nor for case B. But scenarios can be proposed, which cannot be neither refuted, nor strictly validated by the existing 'inversion' models. At this stage, this is a scientific discussion. Case A is supported by several authors, case B was never proposed. We will make things clearer and more consensual in the revised version, by discussing the L&W and V&G models, and including Wanner et al. (2014) modeling as well, as explained above.

The following are some more specific comments:
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 F_CO2,sources = F_CO2,sinks. This is subtly but importantly different from V&G eqn. 4, where V&G 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 F_CO2,hyd are highly uncertain and much debated (as noted above).

We agree. It is not easy to build a model of the whole Earth. Our model limitations will be discussed in more details in the revised version. We already discussed the uncertainties related to the hydrothermal degassing flux. As stated above, our results are weakly dependent on the precise shape of the degassing curve. Furthermore, we used an hydrothermal flux reconstruction proposed by Engebretson (1992) because it is in agreement with the general climatic evolution of the last 65 million years.

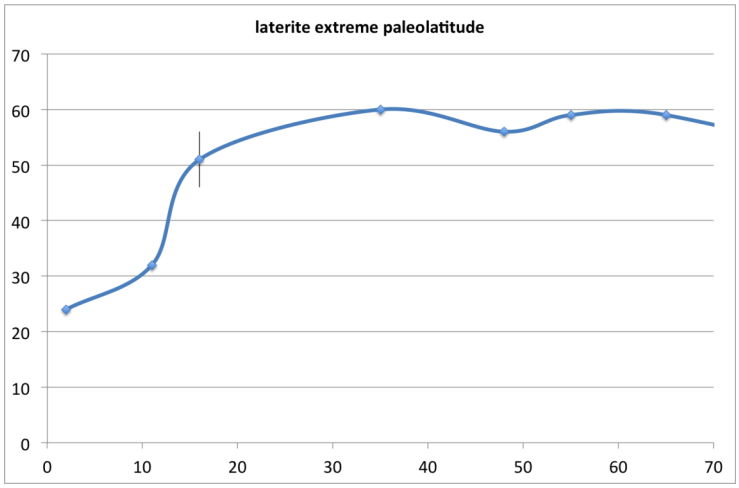
In Section 3.1, V&G argue that dissolved continental fluxes of Li probably did not decrease since 55 Ma. I tend to agree that this is probably the case, but I am not sure the logic as set out by V&G is totally robust. The first reason that V&G cite is the record of other elements and isotopes in seawater, 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. Were there more 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 reviewer tends to agree with our interpretation (more laterite formation during the warm Eocene than today). The compilation of laterite formation by Beauvais and Chardon (2013) clearly shows that the major episode of laterite formation is centered on 55 Ma in West Africa, at the time of the climatic optimum (Zachos et al., 2008) and when West Africa was located in the warm and humid convergence zone. But laterite profiles have been also identified at high latitudes during the same time interval. At least four spikes of lateritic formation are recorded between 55 and 48 Ma at high latitude, the cause of it being identified as a global warming (Retallack, 2008, J. Geol., 116, 558-570). Paleocene high paleolatitude lateritic formations (55°N) have been found in Ireland (Tabor and Yapp, 2005, GCA, 69, 5495-5510). Kaolinite high abundances are also identified in ODP sites 689 and 690 during the early Eocene (Robert and Kennett, 1992, Marine Geology, 103, 99-101). There is thus no doubt that the early Cenozoic was a period of intense kaolinite profile formations.

The same correlation between warm climates and lateritic formation can be identified during the middle Miocene climatic optimum, in Western Africa (Beauvais and Chardon, 2013), in Germany (51° paleolatitude, Schwarz, 1997, Palaeogeogr. Palaeoclim. Palaeoecol., 129, 37-50, in Australia (47° paleolatitude, Schmidt et al., 1983, Palaeogeogr. Palaeoclim. Palaeoecol., 44, 185-202).

Another argument comes from the compilation by Retallack (2010). He shows that the extreme paleolatitudes of laterites was constant around 60° from 65 to 35 Ma. Then it decreases slightly during the MMCO. But the most important point is the drastic decrease of this paleolatitude after the MMCO (15 Ma), exactly at the time where our model riverine Li flux starts to rise sharply. Of course, a latitudinal contraction of the geographic area where lateritic profiles occur is not an unequivocal clue for a decrease in the global volume of kaolinite profiles. Nevertheless, and in the absence of a compilation of those volumes as a function of age, this strongly suggests that our scenario B, which proposes an overall decrease in the Li storage in clays over the Cenozoic, might be geologically supported.

The reviewer raised a good point, and this more argumented discussion and associated references will be included in the revised version.



Extreme paleolatitude reached by lateritic system, as a function of time (Ma) (Retallack, 2010).

It seems to me that the value for C/Li_hyd reported in Table 2 (6.67 x 10ˆ-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/k2? 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.

This will be corrected in the revised version.

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 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 some discussion of them is warranted in this paper, along with some effort to put the current work in the context of these previous papers.

References to these works will be added and discussed, as explained above.

I think it is unnecessarily confusing for V&G to adopt different terminology in their mass balance equations, compared to that used by Bouchez et al. (2013, Am. J. Sc.; which they cite) and also adopted by L&W. In particular, V&G refer to the riverine dissolved flux as δ7Li_riv, which is δ7Li_diss in the Bouchez et al. terminology. Instead, V&G use δ7Li_diss to refer to primary mineral weathering, which is δ7Li_prim in the Bouchez terminology. I think it would help readers not to switch these terms, but rather for V&G to consistently use the same terminology as adopted previously. Or, if V&G feel strongly about their usage, I think they need to at least to explicitly state the new definitions, the differences compared to the papers they cite, and the reasons for these differences.

We will add further explanations about the terminology we use.

V&G do not address the high 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.

Although our model depends on the Li content of the weathered rock, there is no constraint on how these contents may fluctuate globally. The question is not really how do the outcrops of different rocks may have changed over the Cenozoic. The question is how does each rock type contribute to the global weathering flux, according to change in climate and in tectonic settings (both factor being partly linked). This is beyond the capability of our simple model (and this is also true for the L&W model), but is currently explored with coupled 3D-climate/biogeochemical models (Taylor et al., 2013; Lefebvre et al., 2013). Exploring the impact of this on the lithium cycle is a task for the future.