

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 $\delta^7\text{Li}$ record (Misra and Froelich, 2012). Most importantly it does not rely on geochemically unlikely congruent weathering to explain the low seawater $\delta^7\text{Li}$ value observed at the Paleocene-Eocene boundary. Moreover, the authors focus on climate as a potential driver for explaining the change in seawater $\delta^7\text{Li}$, 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 $\delta^7\text{Li}$: A direct proxy for global CO_2 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 $\delta^7\text{Li}$ 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 $\delta^7\text{Li}$ 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 FL_{diss}? 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 FL_{diss} refers to the Li flux associated with primary silicate dissolution only, the first part of equation (6) should read something like $F_{CO_2riv} = 1/k \times (FL_{diss} - FL_{isp})$.

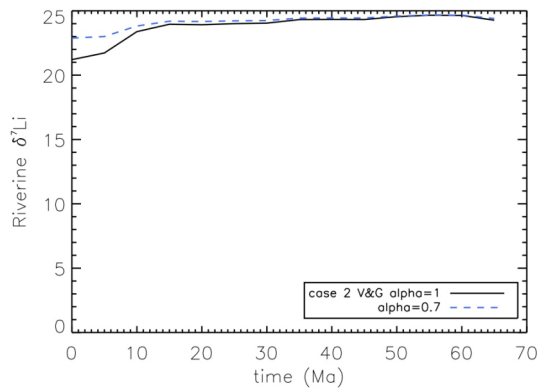
Strictly speaking, silicate dissolution consumes atmospheric CO₂ by the release of base cations on continental waters (Na⁺, Ca²⁺, Mg²⁺, K⁺). In the absence of sulfuric or nitric acid, the charge of those cations is balanced by the negative charge of dissolved HCO₃⁻. Furthermore, at the geological timescale, only Ca²⁺ and Mg²⁺ matter, because neither sodium nor potassium carbonates can precipitate in the ocean. Mg²⁺ 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 CO₂ consumption by fresh silicate rock dissolution is to incorporate cations, mainly Ca²⁺. Kaolinite do not contain base cations. Consequently, it does not limit the CO₂ 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 Ca²⁺ 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 CO₂ consumption. This is why we assume that the CO₂ 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:

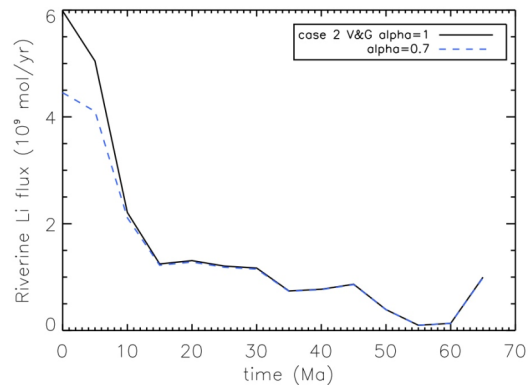
$$F_{riv}^{CO_2} = \alpha F_{diss}^{CO_2} = \alpha/k_1 F_{diss}^{Li}$$

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 $\delta^{7}Li$ of river waters increased” This statement is in contradiction to Wanner et al., (2014) who presented reactive transport model simulations showing that riverine $\delta^{7}Li$ is inversely correlated with saprolite thickness (i.e., low riverine $\delta^{7}Li$ 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 6Li , more clays formed lead to more 6Li depletion into waters, resulting in higher $\delta^{7}Li$ 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 that 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 $\delta^7\text{Li}$ arises from a longer residence time of water in contact with depleted secondary phases if regoliths are thicker. This may decrease riverine $\delta^7\text{Li}$. In our budget model, the formation of secondary phases from fresh bedrock produce an increase of river isotopic composition, because ^6Li 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 $\delta^7\text{Li}$ value

I believe that 1.7‰ is the value reported for the average continental crust (Teng et al., 2009).

In contrast, a value of $0\pm 2\%$ 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)

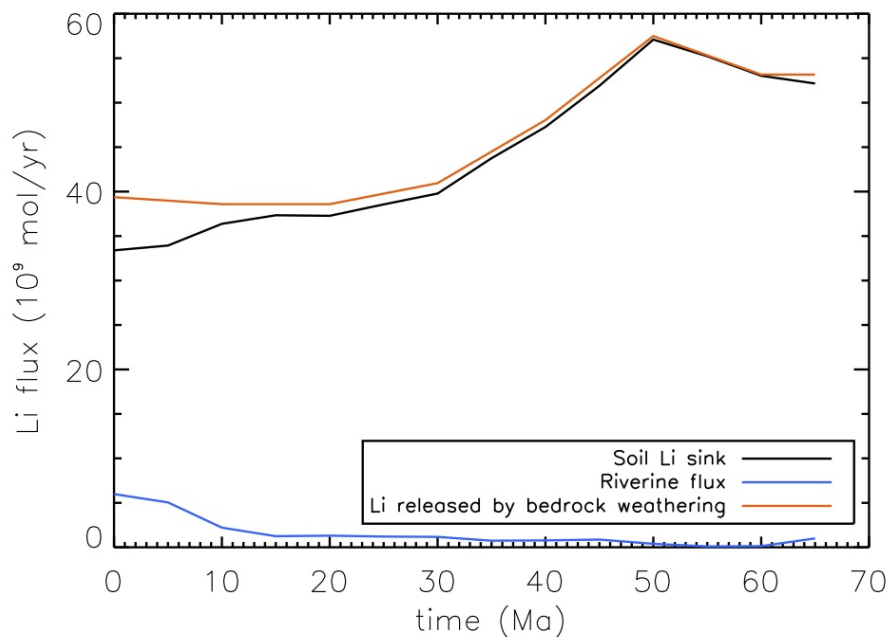
I fully agree that the riverine Li flux likely increased during the Cenozoic. It is consistent with our own reactive transport model simulations (Wanner et al., 2014) as well as with the flux and mass balance calculations performed by Li and West (2014). However, I would like to see a discussion about 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 $\delta^7\text{Li}$ is necessary to explain the seawater $\delta^7\text{Li}$ record, whereas you state that a change in riverine $\delta^7\text{Li}$ 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 $\approx 10-20$ 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 $\delta^{7}\text{Li}$ 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; Kiskurek 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 $\delta^{7}\text{Li}_{\text{riv}}$ 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.

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. Godd ris and Fran ois, 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:

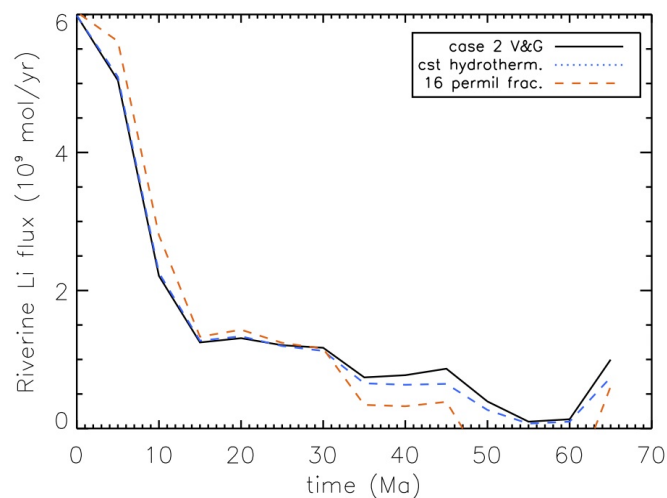
(i) V&G exclude the A solution (Fig. 3a) on the basis that the required decrease in Li dissolved riverine flux with time is not consistent with geological evidence (Section 3.1). I can see the general case for saying Li fluxes probably did not decrease dramatically since 50 Ma. However, I find it problematic 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 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 scenarios 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.

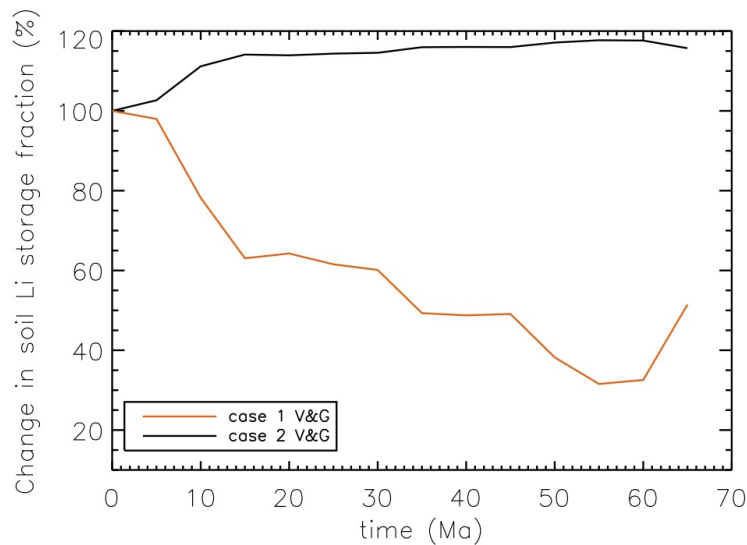
(ii) Although the B solution of V&G is mathematically viable, I estimate that it would imply trapping of ~99% or more of the Li released by primary minerals in secondary phases at 50-60 Ma. V&G haven't reported their model results in a table in this version of the manuscript, but looking at their graphs, at ~55 Ma, $F_{riv} < 1 \times 10^9$ mols/yr, and $F_{sp} > 80 \times 10^9$ mols/yr, requiring that >80/81 of the total Li initially released ($F_{sp} + F_{riv}$) 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 $\sim 1.1 \times 10^{-4}$ (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.

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 $\delta^{7}\text{Li}_{\text{riv}}$ 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 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 (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. 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 $F_{CO_2, sources} = F_{CO_2, sinks}$. 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 $F_{CO_2, hyd}$ 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.

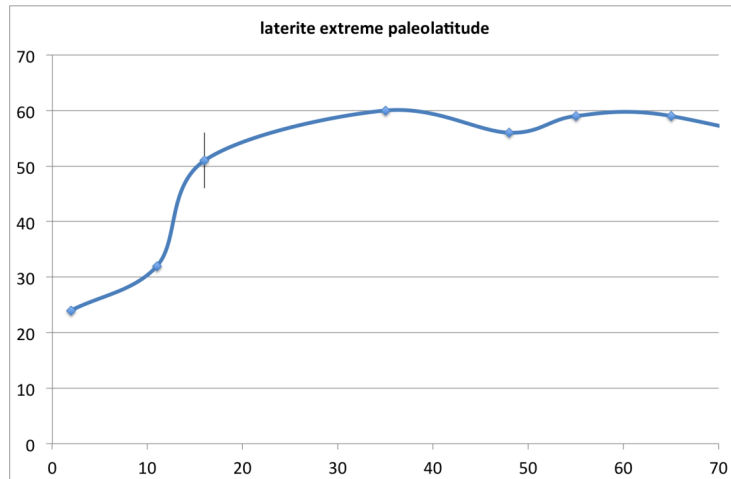
In Section 3.1, V&G argue that dissolved continental fluxes of Li probably did not decrease since 55 Ma. I tend to agree that this is probably the case, but I am not sure the logic as set out by V&G is totally robust. The first reason that V&G cite is the record of other elements and isotopes in seawater, 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 argued 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 (6.67×10^{-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.

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 $\delta^{7}\text{Li}_{\text{riv}}$, which is $\delta^{7}\text{Li}_{\text{diss}}$ in the Bouchez et al. terminology. Instead, V&G use $\delta^{7}\text{Li}_{\text{diss}}$ to refer to primary mineral weathering, which is $\delta^{7}\text{Li}_{\text{prim}}$ 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.

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**A new approach for modeling the Cenozoic oceanic
lithium isotope paleo-variations : the key role of climate**

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Annotated Version

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32

33 **Abstract**

34

35 The marine record of the ocean lithium isotope composition may provide important
36 information constraining the factors that control continental weathering and how they have
37 varied in the past. However, the equations establishing the links between the continental flux
38 of Li to the ocean, its Li isotope composition and the ocean Li isotope composition are under-
39 constrained, and their resolution are related to significant uncertainties. In order to partially
40 reduce this uncertainty, we propose a new approach that couples the C and Li cycles, such
41 that our proposed reconstruction of the Cenozoic Li cycle is compatible with the required
42 stability of the exospheric carbon cycle on geological timescales. The results of this exercise
43 show, contrary to expectations, [that the Cenozoic evolution of the Li isotope composition of](#)
44 [rivers does not have necessarily mimicked the oceanic \$\delta^7\text{Li}\$ rise](#). In contrast, variations in the
45 continental flux of Li to the ocean are demonstrated to play a major role in setting the ocean
46 $\delta^7\text{Li}$. We also provide evidence that Li storage in [secondary phases](#) is an important element of
47 the global Li cycle that cannot be neglected, [in particular](#) during the [early](#) Cenozoic. Our
48 modeling of the published foraminifera record highlight a close link between soil formation
49 rate and indexes recording the climate evolution during the Cenozoic, such as foraminifera
50 $\delta^{18}\text{O}$ and $p\text{CO}_2$ reconstructions. This leads us to propose that climate exerted a dominant
51 control on soil production [rates](#) during the last 70 Ma.

52

53

53 1. Introduction

54

55 Weathering (chemical erosion) of continental Ca-Mg rich silicates serves as a major sink of
56 atmospheric CO₂. However, determining how such weathering has evolved in the past, as a
57 function of climate or tectonic activity, remains a challenge. Filling this gap in our knowledge
58 is essential if we are to understand how global temperature is regulated on geological
59 timescales. The great potential of lithium isotopes to trace alteration processes has recently
60 been highlighted (see e.g. review in Burton & Vigier, 2011). Nevertheless, analytical
61 difficulties have limited their use as a marine paleoproxy. Misra & Froelich (2012)
62 determined the evolution of the lithium isotopic composition of bulk carbonates and
63 planktonic foraminifera over the past 68 Ma. These authors argue that this record reflects
64 ocean-wide variations, and that the 9‰ increase of the marine δ⁷Li from the Paleocene to the
65 present (see figure 1), can be explained by an increase of river δ⁷Li from 3‰ 60 Ma ago, to
66 23‰ at present. To account for such a [rise](#) in riverine δ⁷Li Misra and Froelich (2012) invoke a
67 change of the alteration regime (from a congruent to a weathering- limited regime) and an
68 increase of clay formation (which fractionates Li isotopes) in mountainous - rapidly eroding -
69 areas. This assertion links the secular increase in the marine δ⁷Li record to increasing tectonic
70 uplift and mountain building over the course of the Cenozoic. Under this interpretive
71 framework, continental weathering during the early Paleogene (≈ 60 Myrs ago) was
72 characterized principally by high dissolution rates of continental rocks and relatively low rates
73 of clay formation and transport. Such a weathering regime offers a mechanism for producing
74 low δ⁷Li values in rivers, close to that of the continental crust, because dissolution is not
75 accompanied by significant Li isotope fractionation. Later in the Cenozoic, as tectonic activity
76 intensifies, incongruent weathering and clay formation is supposed to become more
77 significant, leading to a shift to larger riverine δ⁷Li.

78 However, several lines of evidence call this interpretation of the seawater record into
79 question, and in particular the notion that low δ⁷Li values in rivers of the Cretaceous could be
80 sustained by predominately congruent weathering ([Wanner et al., 2014](#)). Indeed, a
81 congruency of the weathering process, that would correspond to small rates of clay formation
82 or soil production, at 60 Ma is not supported by the occurrence of thick weathering profiles
83 found at this period of time (e.g. Beauvais & Chardon, 2013; Tavlan et al., 2011; Meshram &
84 [Randiv, 2011](#)). [In particular, the compilation of laterite formation by Beauvais and Chardon](#)
85 [\(2013\) shows that a major episode of laterite formation is centered on 55 Ma in West Africa.](#)

86 [at the time of the climatic optimum \(Zachos et al., 2008\) and when West Africa was located](#)
87 [in the warm and humid convergence zone. Laterite profiles have also been identified at high](#)
88 [latitudes during the same time interval. At least four spikes of lateritic formation are recorded](#)
89 [between 55 and 48 Ma the cause of it being identified as global warming \(e.g. Retallack,](#)
90 [2010; 2014\).](#) A compilation of about 80 ODP or DSDP core sites indicate that the deep
91 seawater during the Paleocene exhibited low $\delta^{18}\text{O}$ values, with benthic foraminifera $\delta^{18}\text{O}$
92 values between 3 and 4 ‰ lower than at present (Zachos et al., 2001). This feature is
93 interpreted as much warmer climatic conditions, in agreement with recent reconstructions of
94 atmospheric $p\text{CO}_2$ at 60 Ma, ranging between 400 and 1000 ppmv (Beerling & Royer, 2011).
95 These conditions have favored the formation of thick weathering profiles, in particular of
96 lateritic regolith mantles rich in kaolinite and/or bauxite. These resistant phases are depleted
97 in major cations playing a key role in the carbon cycle (such as Ca and Mg), but they contain
98 significant amounts of Li. Our compilation of Li levels in kaolinite-rich samples (Table 1)
99 shows that they are - on average - similar to the Li content estimated for the continental crust
100 granites (22ppm \pm 4ppm, Teng et al., 2009). They may therefore have played a key role in the
101 continental Li cycle. Li-containing regoliths provide empirical evidence against the idea that
102 congruent weathering prevails during warm intervals of Earth history driving riverine $\delta^7\text{Li}$ to
103 values similar to average upper crust.

104 In this study, we propose a new modeling approach of the seawater record that consists in
105 coupling a simple mathematical description of the carbon and the lithium exospheric budget,
106 throughout the Cenozoic. The objective is not to produce an exhaustive study of the impact of
107 each parameter implied in the Li and the C cycle, but rather to show that for a given set of
108 parameters consistent with published estimations, there is an alternative solution that can
109 explain the Cenozoic $\delta^7\text{Li}$ oceanic variations.

110 Our model takes into account the changes in Li flux coming from the continents in response
111 to a balance between 1/ dissolution rates of continental rocks releasing Li in waters and 2/
112 temporary storage of Li into secondary phases formed in weathering profiles. Since lithium
113 isotopes fractionate during clay mineral accumulation (e.g. Huh et al., 2001; Kisakurek et al.,
114 2004; Rudnick et al., 2004), soil formation rate is expected to drive the Li isotope
115 composition of rivers. One illustration is that, at present, the mean $\delta^7\text{Li}$ value of the
116 continental runoff (+23‰; Huh et al., 1998) is much higher than the average $\delta^7\text{Li}$ value
117 estimated for the continental crust granites (+2 \pm 4‰, Teng et al, 2009). Since Li isotopes do
118 not fractionate during dissolution, this difference is best explained by isotope fractionation

119 during the formation of secondary phases (Vigier et al., 2009; von Strandmann et al., 2010;
120 Bouchez et al., 2013). Consequently, at present, at the world-wide scale, a significant part of
121 the Li released by continental dissolution is stored in ⁶Li-rich soils, resulting in heavy
122 signatures (⁷Li-rich) in rivers. Experimental investigations, as well as soil studies support
123 these findings (e.g. Wimpenny et al., 2010; Vigier et al., 2008; Lemarchand et al, 2010).
124 Thus, we explore how Li storage in soils at the global scale has affected the ocean $\delta^7\text{Li}$ value,
125 as well as the potential of ocean $\delta^7\text{Li}$ to quantify the balance between physical denudation and
126 chemical alteration and its variation throughout the Cenozoic.

127

128 **2. Model equations and basics**

129

130 *2.1. Seawater isotopic balance*

131

132 The two main sources of dissolved lithium to the ocean (oc) are river waters (riv) and high
133 temperature hydrothermal fluids (hyd) (see Huh et al., 1998 and a detailed review in
134 Tomascak, 2004 and in the supplementary material of Misra and Froelich, 2012). The main
135 sink of oceanic lithium is its incorporation into authigenic phases, in particular marine clays
136 which are the marine phases the most enriched in Li (Chan et al. , 2006). The seawater
137 isotopic mass balance can thus be written as :

138

$$139 \quad M_{oc}^{Li} \cdot d\delta_{oc}/dt = F_{riv}(\delta_{riv}-\delta_{oc})+F_{hyd}(\delta_{hyd}-\delta_{oc})-F_{clay}(\delta_{oc}-\Delta_{oc}-\delta_{oc}) \quad (1)$$

140

141 where F is for the Li flux, and δ_{riv} δ_{oc} and δ_{hyd} are for the $\delta^7\text{Li}$ values of rivers, ocean and
142 hydrothermal fluids respectively. Δ_{oc} represents the absolute value of the fractionation factor
143 of the Li isotopes during marine secondary phase formation. In [the literature](#), this factor [is](#)
144 [negative \(preferential enrichment of the light ⁶Li isotope\) and](#) ranges between -10 and -25%
145 depending on the temperature at which authigenic phases are being formed (Chan et al, 1992;
146 1993; Vigier et al., 2008).

147

148 The residence time of Li in the ocean is equal to 1 million years. Given that we are exploring
149 the time evolution of its isotopic cycle over the whole Cenozoic (10^7 year timescale), we can
150 assume steady-state for both the elemental (i.e. all the Li carried by rivers and released by
151 hydrothermal activity into the ocean is removed through authigenic clay formation: $F_{riv} + F_{hyd}$

152 = F_{clay}) and isotopic Li cycles. [The steady-state hypothesis is only valid for a timescale of](#)
153 [several million years \(at least three times the Li residence time in the ocean\).](#)

154

155 Equation (1) becomes:

$$156 \quad F_{\text{riv}}(\delta_{\text{riv}} - \delta_{\text{oc}}) + F_{\text{hyd}}(\delta_{\text{hyd}} - \delta_{\text{oc}}) + F_{\text{riv}} \cdot \Delta_{\text{oc}} + F_{\text{hyd}} \cdot \Delta_{\text{oc}} = 0 \quad (2)$$

157

158 Consequently, we can solve the above equations for δ_{oc} :

$$159 \quad \delta_{\text{oc}} = (F_{\text{riv}}\delta_{\text{riv}} + F_{\text{hyd}}\delta_{\text{hyd}} + \Delta_{\text{oc}}(F_{\text{riv}} + F_{\text{hyd}})) / (F_{\text{riv}} + F_{\text{hyd}}) \quad (3)$$

160

161 where present day published values for F_{riv} , F_{hyd} and Δ_{oc} are reported in Table 2. We consider
162 that the hydrothermal flux during the Cenozoic decreased slightly as a function of time,
163 following the curve described in Engebretson et al. (1992), based on variations of subduction
164 rates and mid-ocean ridge volume. This trend is currently used in numerical modeling of the
165 global carbon cycle and appears to be consistent with the Cenozoic climatic evolution
166 (Berner, 2004; Lefebvre et al., 2013).

167

168 Basically, equation 3 has two unknowns: $F_{\text{riv}}^{\text{Li}}$ and δ_{riv} . In previous studies (Hathorne and
169 James, 2006; Misra & Froelich, 2012), river $\delta^7\text{Li}$ has been interpreted as co-varying in a
170 straightforward way with the ocean $\delta^7\text{Li}$. However, one equation is not enough for two
171 independent unknowns. In contrast to the a priori expectation, the variation of the ocean $\delta^7\text{Li}$
172 composition during the Cenozoic may not reflect riverine $\delta^7\text{Li}$ variations in a straightforward
173 way. The reason for this is that it strongly depends on the continental Li flux too, which is
174 likely to have been strongly affected by variation in continental weathering rates during this
175 period of time. One purely theoretical example of the influence of the Li continental flux is
176 illustrated in Figure 2. This simulation shows that the 0-65Ma foraminifera $\delta^7\text{Li}$ record
177 (shown in figure 1) can still be fitted by imposing a constant river $\delta^7\text{Li}$ throughout the
178 Cenozoic, and using parameters values which are consistent with published data (Table 2).
179 We fixed the δ_{riv} ($\delta^7\text{Li}$ in rivers) to its present-day value (23‰). This is an extreme and
180 unlikely scenario because it does not account for change in the isotope fractionation due to
181 continental weathering. Indeed, the riverine $\delta^7\text{Li}$ is expected to vary as a function of the
182 relative importance of dissolution rate and clay formation rate (e.g. Bouchez et al., 2013).
183 However, this simulation shows that, by taking into account the Li ocean budget only, the
184 system of equations is under-constrained and it is not possible to calculate the temporal

185 variations of riverine $\delta^7\text{Li}$ without making assumptions about the link between $F_{\text{riv}}^{\text{Li}}$ and δ_{riv} .
186 It also shows that low seawater $\delta^7\text{Li}$, as highlighted by early Eocene foraminifera can be
187 compatible with a high $\delta^7\text{Li}$ value of the riverine flux. Our result shows therefore that low
188 $\delta^7\text{Li}$ in the ocean does not systematically imply low river $\delta^7\text{Li}$. The temporal variations of the
189 riverine Li flux also need to be established. In the following, we add constraints on this aspect
190 and the Li cycle, by coupling it to the carbon cycle.

191

192 2.2. Walker paleothermostat

193

194 The Walker paleothermostat (Walker et al., 1981) implies that, at the million year scale, the
195 consumption of carbon by silicate weathering ($F_{\text{riv}}^{\text{CO}_2}$) closely balances the release by
196 volcanic degassing (assumed to be proportional at first order to the seafloor spreading rate,
197 and hence to the hydrothermal activity) ($F_{\text{hyd}}^{\text{CO}_2}$), a condition absolutely needed to avoid
198 unrealistic atmospheric CO_2 fluctuations (Godderis & François, 1995; Kump & Arthur,
199 1997):

$$200 F_{\text{hyd}}^{\text{CO}_2} = F_{\text{riv}}^{\text{CO}_2} \quad (4)$$

201

202 During high temperature water-rock interactions, Li is known to be highly mobile, as
203 reflected by the large Li concentrations found in hydrothermal fluids located in mid-ocean
204 ridges (ppm level, Chan et al., 1994; Foustoukos et al., 2004; Mottl et al., 2011), and which
205 are ~ 3 orders of magnitudes greater than in river waters or seawater. Consequently, we
206 consider that the amounts of Li released by hydrothermal process is proportional to the carbon
207 flux released into the ocean:

208

$$209 F_{\text{hyd}}^{\text{CO}_2} = k_2 F_{\text{hyd}}^{\text{Li}} \quad (5)$$

210

211 with $k_2 = (C/\text{Li})$ of hydrothermal fluids (Table 2)

212 In contrast with hydrothermal conditions, Li is much less "mobile" on the continents,
213 as reflected by low Li contents in river waters (ppb level) while granites (the main source of
214 river Li) are enriched in Li compared to oceanic crust. Indeed, first, thermodynamic laws
215 indicate that dissolution rate is lower at lower temperature. Additionally, it is observed that
216 most of the Li carried by rivers to the ocean is mainly located in the particulate load ($>70\%$,
217 e.g. Millot et al., 2010), while the dissolved Li represents only a minor proportion. This is

218 consistent with the fact that Li can be significantly incorporated into the structure of
 219 secondary minerals, mainly clays. As a consequence, the flux of dissolved Li carried by rivers
 220 may not be proportional to the flux of CO₂ consumed during the leaching or dissolution of
 221 continental mineral phases. The relationship linking the flux of lithium carried by rivers and
 222 the flux of atmospheric CO₂ consumed by mineral dissolution becomes:

$$223 \quad F_{\text{riv}}^{\text{CO}_2} = 1/k_1 \cdot F_{\text{diss}}^{\text{Li}} = (F_{\text{riv}}^{\text{Li}} + F_{\text{sp}}^{\text{Li}}) / k_1 \quad (6)$$

225 $F_{\text{riv}}^{\text{Li}}$ and $F_{\text{sp}}^{\text{Li}}$ being the flux of lithium in river waters and in secondary phases respectively,
 226 and $F_{\text{diss}}^{\text{Li}}$ the flux of Li released into continental waters during the dissolution of continental
 227 rocks ($F_{\text{riv}}^{\text{Li}} = F_{\text{diss}}^{\text{Li}} - F_{\text{sp}}^{\text{Li}}$). k_1 is calculated assuming that dissolution of continental rocks
 228 release Li, Mg and Ca congruently. Also, we consider that 1 mol of atmospheric CO₂ is
 229 consumed by the dissolution of 1 mol of Mg+Ca present in continental rocks (accounting for
 230 the subsequent carbonate precipitation in the ocean) (Berner, 2004). Consequently, $k_1 = \text{Li}_{\text{UCC}}$
 231 / (Ca + Mg)_{UCC} (UCC being the Upper Continental Crust, Table 2).

232 If present-day conditions might reflect a recent disequilibrium due to the last glaciation
 233 (Vance et al., 2009), at the Cenozoic timescale, formation of thick weathering profiles with
 234 significant residence time (>0.5Ma) are likely to have impacted the Li cycle. We assume that
 235 most of secondary phases present in these profiles are largely depleted in cations, in particular
 236 in Ca and Mg, and therefore do not affect significantly the carbon budget. [This is a first order](#)
 237 [approximation. Indeed, laterite in which the largely dominant clay phase is Mg-Ca free](#)
 238 [kaolinite, covers only 30% of the continental surfaces. However, owing to their thickness,](#)
 239 [they constitute about 85% of the global continental pedogenic cover \(Nahon, 2003\),](#)
 240 [supporting the above assumption.](#)

241
 242 Combining equation (4) (5) and (6) we obtain the following relationship:

$$243 \quad F_{\text{riv}}^{\text{Li}} = k_1 k_2 F_{\text{hyd}}^{\text{Li}} - F_{\text{sp}}^{\text{Li}} \quad (7)$$

245
 246 where the flux of riverine Li is a function of both the hydrothermal flux and of the [secondary](#)
 247 [phase](#) formation rate on the continents.

248
 249 *2.3. Riverine $\delta^7\text{Li}$*

250

251 All published studies indicate the existence of a strong isotope fractionation during the
 252 formation of secondary phases, such as clays or Fe oxides, always in favor of the light isotope
 253 (⁶Li). At periods when the soil production and thickness [increased](#) in the past [due to increase](#)
 254 [rate of secondary phase formation](#), we therefore expect that the δ⁷Li of river waters increase,
 255 since more ⁶Li is incorporated and stored into soils. In fact, the riverine δ⁷Li is the result of
 256 the competition (e.g. Bouchez et al., 2013, [Vigier et al., 2009](#)) between the isotopically
 257 congruent dissolution of fresh bedrock, and the precipitation of secondary phases with an
 258 isotope fractionation Δ_{land} (Table 2), such that:

$$259 \quad F_{\text{riv}}^{\text{Li}} \delta_{\text{riv}} = \delta_{\text{UCC}} F_{\text{diss}}^{\text{Li}} - F_{\text{sp}}^{\text{Li}} (\delta_{\text{riv}} - \Delta_{\text{land}}) \quad (8)$$

261 with δ_{UCC} being the average δ⁷Li value estimated for the upper continental crust (Table 2).

262 Given that $F_{\text{diss}}^{\text{Li}} = F_{\text{riv}}^{\text{Li}} + F_{\text{sp}}^{\text{Li}}$, equation (8) becomes:

$$263 \quad \delta_{\text{riv}} = \delta_{\text{UCC}} + (F_{\text{sp}}^{\text{Li}} \Delta_{\text{land}}) / (F_{\text{riv}}^{\text{Li}} + F_{\text{sp}}^{\text{Li}}) \quad (9)$$

264
 265 This equation states that , if $F_{\text{sp}}^{\text{Li}} = 0$, then δ_{riv} equals δ_{UCC}. Otherwise, δ_{riv} is higher than δ_{UCC}.
 266 To date the published values of δ⁷Li of most rivers (e.g. Huh et al., 1998, Millot et al., 2010;
 267 Kusakurek et al., 2004) are significantly greater than the δ⁷Li estimated for UCC (2‰ , Teng
 268 et al. 2009), and thus are consistent with equation (9).
 269
 270

271 2.4. Method for solving the model

272
 273 We assume that the foraminifera δ⁷Li reflect the ocean δ⁷Li, as assumed in Misra & Froelich
 274 (2012) and in Hathorne & James (2006). We consider that potential vital effects, responsible
 275 for changes of Li isotope fractionation during foraminifera growth may explain some
 276 observed rapid (<0.5Ma) changes of foraminifera Li isotope compositions, but we do not take
 277 into account these effects since the model aims at working at the multi million scale only. A
 278 moving average of the oceanic lithium isotopic data is calculated, with a window width of 5
 279 millions of years, [since the isotopic steady-state is valid for a timescale of at least three times](#)
 280 [the Li residence time in the ocean](#) (see figure 1). This data smoothing [therefore](#) ensures the
 281 validity of the steady-state hypothesis and removes [all](#) short term fluctuations potentially
 282 related to vital effects.
 283

284

285 The equations describing the seawater isotopic budget (eq. 3), the paleothermostat (eq.
286 7), and the riverine isotopic budget (eq. 9) define a system of equations where the unknowns
287 are the riverine Li flux as a function of time (F_{riv}^{Li}), the storage flux of Li in soils (F_{sp}^{Li}), and
288 the riverine δ^7Li (δ_{riv}). It can be reduced to the following quadratic equation :

289

$$290 \quad A_1 (F_{riv}^{Li})^2 + (\delta_{oc} - \Delta_{oc} - \delta_{UCC} - \Delta_{land}) F_{riv}^{Li} - A_2 = 0. \quad (10)$$

291

292 Where A_1 and A_2 are equal to :

$$293 \quad A_1 = \Delta_{land} / (k_1 k_2 F_{Hyd}^{Li}) \quad (11)$$

$$294 \quad A_2 = F_{Hyd}^{Li} (\delta_{hyd} - \delta_{oc} + \Delta_{oc}) \quad (12)$$

295

296 The values for the various parameters used in the model are described in Table 2. As long as
297 the discriminant of eq. 10 is strictly positive, eq. 10 has two solutions for F_{riv}^{Li} . This means
298 that two radically different histories of F_{riv}^{Li} can both explain the rise of the Li isotopic
299 composition of seawater.

300

301 [2.5. Comparison with other modeling methods](#)

302

303 [Recently, two modelings of the Cenozoic \$\delta^7Li\$ variations, different from Misra and Froelich](#)
304 [\(2012, 2014\) \(section 1\) have been proposed. Wanner et al. \(2014\) focused on a reactive](#)
305 [transport model in order to simulate the Li isotopic composition and content of continental](#)
306 [waters. Weathering reactions by sub-surface waters are simulated, considering a prescribed](#)
307 [thick regolith which already contains altered material \(kaolinite and goethite\), above a fresh](#)
308 [granite. Kinetic reactions based on transition state theory are used for calculating both the](#)
309 [dissolution and precipitation of mineral phases. River water chemistry is then considered to](#)
310 [be a simple dilution of these sub-surface waters having reacted with previously formed](#)
311 [profiles. Overall, the Wanner et al. \(2014\) model is designed to simulate finely the time](#)
312 [evolution of an already existing regolith profile and its impact on the riverine Li content and](#)
313 [isotopic composition. As acknowledged by the authors, the fit of the Cenozoic oceanic \$\delta^7Li\$](#)
314 [curve cannot be computed as it would require the accurate knowledge of the Cenozoic climate](#)
315 [and runoff variations, to calculate the Li flux to the ocean as well as its isotopic composition.](#)

316 [The Wanner et al. \(2014-\) model is a process-based model, but at this stage, it cannot account](#)
317 [for global budget.](#)

318
319 [Li and West \(2014\) proposed 12 different simulations for fitting the Cenozoic ocean \$\delta^7\text{Li}\$,](#)
320 [focusing their effort on potential variations of the oceanic Li sink and how this could have](#)
321 [affected the ocean \$\delta^7\text{Li}\$. They consider that the two major sinks of ocean Li are marine](#)
322 [authigenic aluminosilicate clays \(during reverse weathering, at low temperature\), and](#)
323 [removal into oceanic crust during its alteration by circulating fluids of moderate to high](#)
324 [temperatures. Both sinks are considered to be associated with a constant isotope fractionation](#)
325 [factor throughout the Cenozoic, but a varying proportion of both is considered to influence](#)
326 [the Li and \$\delta^7\text{Li}\$ removal flux. Then, a steady-state equation is applied to the ocean, identical to](#)
327 [the one used here, and different scenarios are tested to explore the impact of the mathematical](#)
328 [formulation of the oceanic Li sinks. Changes of river Li flux are assumed to be dependent on](#)
329 [the chemical weathering fluxes calculated by another model \(Li and Elderfield, 2013\), or](#)
330 [following the isotope balance method developed by Bouchez et al. \(2013\). Hydrothermal Li is](#)
331 [estimated from the reconstruction of spreading rate \(Muller et al., 2008; Rowley, 2002\). No](#)
332 [direct coupling with the carbon cycle is made.](#)

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333
334 [At this stage, it is important to underline that, by coupling Li and C budgets, the solving of](#)
335 [our model equations does not require additional or independent assumptions for the](#)
336 [continental fluxes \(dissolved and particulate\) during the Cenozoic. Furthermore, our model is](#)
337 [only based on budget equations \(for Li and C\), and does not include any assumption on the](#)
338 [dependence of fluxes on environmental conditions. The solid Earth degassing is extracted](#)
339 [from Egebreton \(1992\). Although more recent reconstructions have been published, it has](#)
340 [been shown recently that the Egebreton's curve is in good agreement with the Cenozoic](#)
341 [climate history \(itself reconstructed using a coupled 3D climate-carbon model, see Lefebvre](#)
342 [et al., 2013\). The precise Cenozoic history of the solid Earth degassing weakly influences our](#)
343 [results.](#)

344
345
346

347 **3. Results and discussion**

348

349 **3.1 Paleo-variations of continental weathering**

350

351 Two solutions have thus been found for the Cenozoic (represented in figure 3A and 3B). The
352 first solution (figure 3A) implies an increase of the riverine $\delta^7\text{Li}$ over the Cenozoic,
353 associated to a decrease of riverine Li flux with time. This first solution is close to the
354 scenario described in details by Misra & Froelich (2012), arguing for an increasing
355 contribution of orogenesis on silicate dissolution, clay formation and CO_2 consumption
356 towards recent time. In this scenario, sequestration of lithium in clays increased from the past
357 towards the present day.

358 Our model results demonstrate that a second scenario can also explain the Cenozoic Li
359 isotope record. Indeed, figure 3B shows that the $\delta^7\text{Li}$ paleorecord mainly reflects an increase
360 of the riverine Li flux through the Cenozoic. As illustrated in figure 4, this increase is not due
361 to an increase in the dissolution rate of the silicate lithologies, but is mostly due to the
362 decrease of Li storage in secondary phases stored in soils. Most Li-rich secondary phase are
363 considered to be formed within soil and lateritic profiles, and even if some have the time to be
364 formed during the river transport, this fraction is likely minor compared to the formation of
365 thick soils and kaolinite-rich laterite. Therefore, we consider that most of the Li storage
366 during silicate alteration occur in soils.

367 In order to test the robustness of our result, we performed two different simulations, using 1/
368 the whole set of equations (for both C and Li, see section 2), and 2/ an imposed variation of
369 δ_{riv} that is arbitrarily forced to increase linearly from 15‰ at 65 Ma to 23‰, its present day
370 value (in that case, only the Li budget is solved, not C). Both simulations lead to similar
371 trends, where Li_{soil} decrease as a function of time (see Figure 4). This strongly suggests the
372 robustness of the observed decrease, and also confirms that the Li isotope composition of
373 rivers plays only a minor role in the ocean isotopic variation. Overall, these results show that
374 soil Li storage was high from 65 to 50 Myr, and then decreased continuously until its
375 stabilization at about 20 Myrs ago (Figure 4).

376 In order to be more quantitative, check the consistency of these results and compare them to
377 other proxies, we estimated the corresponding soil formation rates, assuming a Li
378 concentration of 25ppm, which corresponds to an average soil Li concentration, including
379 data shown in Table 1. This is a first approximation because secondary phase formation rate
380 (calculated from Li data) may not strictly correspond to soil formation rate. Also, the
381 estimated average soil Li content may be associated with a large error, as there are currently
382 only few data. It may also have varied as a function of time, although this is not supported by
383 the relative narrow range of Li concentration of the most abundant clays. Nevertheless, this

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384 | assumption allows us to assess if the order of magnitude for [the](#) fluxes extracted from our
385 | model makes sense. Also, a compilation of Li contents for the most abundant low-T
386 | continental clays show that the average Li value is not so different from one type of clay to
387 | another (Tardy et al., 1972; Table 1). During the Cenozoic, we thus estimate that soil
388 | formation rate ranged from $2.2 \cdot 10^{19}$ kg/Ma to a present-day value of $1.3 \cdot 10^{19}$ kg/Ma, i.e.
389 | $2.2 \cdot 10^{10}$ t/yr to $1.3 \cdot 10^{10}$ t/yr. For comparison, Syvitski et al. (2003) estimated a present-day
390 | global physical denudation rate of $2 \cdot 10^{10}$ t/yr. [The Syvitski denudation rate includes](#)
391 | [secondary phases and fresh minerals but the most important here is that both orders of](#)
392 | [magnitude are similar, and not totally at odd.](#) Reconstitution of paleo-denudation rate during
393 | the Cenozoic are controversial (e.g. Willenbring & von Blanckenburg, 2010), but given the
394 | uncertainties typical of global scale estimations, it is worth noting that the calculated soil
395 | formation falls quite close (less than an order of magnitude difference) to the global
396 | denudation estimate, indicating that our calculations - based on C and Li cycles and published
397 | values for corresponding parameters - make sense. [Considering the uncertainties on both](#)
398 | [estimations, a strict comparison between both numbers \(physical and chemical erosion rates\)](#)
399 | [in order to determine if the erosion regime has globally remained close to steady-state \(where](#)
400 | [denudation rate and soil production rates are equal\) during the Cenozoic does not appear to be](#)
401 | [relevant yet.](#)

402

403 | **3.2 Assessing the role of climate**

404

405 | Except for the last few Ma, the paleo-reconstruction of soil formation rate during the
406 | Cenozoic is remarkably parallel to the $\delta^{18}\text{O}$ values measured in benthic foraminifera (Zachos
407 | et al., 2001, see figure 5B). This strongly suggests a major role of climate on soil
408 | development at the global scale. When the climate gets cooler, soil formation rates decrease.
409 | A potential increase of weathering rates due to orogenesis and mountain building during the
410 | Cenozoic is therefore not able to compensate the role of temperature. In the open debate
411 | concerning the controls of continental chemical erosion rates at global scale over the
412 | Cenozoic, Li isotopes yield good evidence of the predominance of climate over mechanical
413 | erosion. Specifically the fact that soil formation rates predicted by the model parallel the
414 | global benthic oxygen isotope record shows that the impact of orogenesis is not strong
415 | enough to counter-balance the impact of temperature decrease.

416 | More closely inspecting the comparison between soil formation rate, $\delta^{18}\text{O}$ and pCO_2 paleo-
417 | variations reveals four remarkable features:

418 1/ High soil formation rates during the Paleocene and Early Eocene, coincides with
419 high $p\text{CO}_2$ estimations (Beerling and Royer, 2011) as well as low foraminifera $\delta^{18}\text{O}$ values.
420 This strongly suggests that weathering rates were high because of climatic conditions
421 favoring both dissolution of silicate rocks and formation of secondary minerals and laterites.
422 [In order to explain the high riverine \$d^7\text{Li}\$ values associated to low Li flux at this period of](#)
423 [time \(see Figure 3B\), our budget equations require a massive transformation of fresh rocks](#)
424 [into regolith. An important soil production also requires important weathering rates,](#)
425 [consistent with high estimated atmospheric \$p\text{CO}_2\$ levels. This intense weathering leads to](#)
426 [worldwide production of thick lateritic profiles, which is evidenced in many parts of the](#)
427 [world \(e.g. Beauvais and Chardon, 2013; Retallack, 2010; Tabor and Yapp, 2005; Robert and](#)
428 [Kennett, 1992\).](#)

429 2/A sharp decrease of soil formation rate coeval with a sharp increase in foraminifera
430 $\delta^{18}\text{O}$ during the Eocene until the beginning of the Oligocene. This co-variation suggests a
431 predominant role of climate cooling on continental soil production. However, during this
432 period of time, we cannot exclude a global thinning of soils by mountain building and
433 orogenesis. Steeper slopes, higher relief, and increasing impact of landslide contribute
434 significantly to reduce the world average soil thickness.

435 3/A stabilization of the weathering rates between 30 and 10Ma, which matches the
436 plateaus exhibited by $p\text{CO}_2$ (not shown here, but see Beerling and Royer, 2011) and $\delta^{18}\text{O}$
437 proxies.

438 4/ A decoupling between soil formation rate, benthic foraminifera $\delta^{18}\text{O}$ and physical
439 denudation rate during the Quaternary period. Indeed, both soil formation rates and $p\text{CO}_2$
440 estimates remain globally stable during this period. However, foraminifera $\delta^{18}\text{O}$ and
441 denudation rates (e.g. Hay et al., 1988) show significant variations, consistent with the
442 development of a cool climate and glaciations. [Reconstructions of \$^{10}\text{Be}/^9\text{Be}\$ in the ocean also](#)
443 [suggest a constancy of the continental weathering rates for the last 5-10 Ma and have](#)
444 [questioned the relationship between physical and chemical erosion rates \(Willenbring and von](#)
445 [Blanckenburg, 2010\).](#) Our results suggest that the recent climatic variations were not strong
446 enough to affect the Li cycle, as evidenced by constant foraminifera $\delta^7\text{Li}$ value during the last
447 5Ma. The other possibility is that the present-day residence time of Li in the ocean is
448 underestimated and the chemical - and potentially physical - disturbances related to
449 Quaternary glaciations did not have time yet to significant affect its oceanic budget.

450

451 3.3 Open questions

452

453 Our result for the Paleocene/Eocene boundary differs from previous modelings in two
454 ways: first, the low ocean $\delta^7\text{Li}$ values at the P/E boundary may not necessarily require low
455 riverine $\delta^7\text{Li}$ values, as previously considered in Wanner et al., (2014), in Misra and Froelich
456 (2012) and in Li and West (2014). Secondly, at a period of time where weathering profiles are
457 abundant and thick, Wanner et al. (2014) reactive transport model shows that low riverine
458 $\delta^7\text{Li}$ such as observed at the Paleocene-Eocene boundary can be explained by predominant
459 dissolution of previously formed secondary phases occurring in pre-formed thick regoliths
460 (rich in kaolinite and goethite) (see section 2.5). The inverse relationship between regolith
461 thickness and riverine $\delta^7\text{Li}$ arises from a longer residence time of water in contact with
462 depleted secondary phases during periods characterized by weak tectonic- activity and low
463 physical erosion rates. In contrast, our model, which is based on budget equations only,
464 implies that the formation of secondary phases from fresh bedrock produce an increase of
465 river $\delta^7\text{Li}$, because ^6Li is preferentially stored in regolith in formation.

466 Future studies should merge both methods such that transformation of the fresh
467 bedrock into regolith and the building of thick weathering profiles can be accounted for, as
468 well as the reactivity of the regolith itself.

469

470 The amount of published Li concentrations in various types of clay is still too limited
471 to estimate precisely the Li mobility at the continental scale. At present, river particles carry
472 more than 80% of the river total Li flux (calculation based on discharge and fluxes published
473 by Gaillardet et al., 1999 and published average Li concentration for river water and
474 suspended particles, Huh et al., 1998; 2001; Kisakurek et al., 2005; Millot et al., 2010;
475 Dellinger et al., 2014). At 55Ma, the Li storage in soils is pretty close to 100% (following
476 solution B). This corresponds precisely to the longest and one of the most intense weathering
477 events of the Cenozoic in western Africa (Beauvais and Chardon, 2013), and probably
478 elsewhere in the world (Rettalack, 2010). Conversely, case A predicts that only 20% of Li is
479 retained during this event. Constraining more precisely the role of Li-rich kaolinite formation
480 in soils and laterites would certainly add precious information to the debate. A recent study of
481 Hawaiian basaltic soil chronosequence (Ryu et al., 2014) show that Li is retained at 100% in
482 soil layers rich in kaolinite, which further supports their critical role, but more investigation at
483 larger scale is now required.

484
485 In our modeling, the hydrothermal carbon flux is assumed to be strictly compensated
486 by continental silicate weathering. The potential role of other sources/sinks of carbon has
487 been neglected at this stage, in particular the influence of metamorphism and of organic
488 matter burial. Indeed, disequilibria in the organic carbon subcycle may alter the
489 proportionality between the total CO₂ consumption by continental silicate weathering and the
490 CO₂ release hydrothermal activity. In the case of the strontium cycle for instance, it is well
491 known that such additional processes may produce non negligible fluctuations of the oceanic
492 isotopic composition (Goddéris and François, 1995). In the case of the Li cycle, these
493 processes are not expected to influence significantly the Li fluxes and their isotope signatures.
494 However, change of carbon fluxes can potentially produce alteration of the Li isotopic
495 composition of the ocean. This is an important field for future investigations. The objective
496 here was to decipher the first order control factors on the time evolution of the Li cycle. The
497 calculated scenarii must be seen as a background history, neglecting at this stage processes
498 that could modulate the model output around the proposed long term averaged evolution.

499
500 Although our model depends on the Li content of the continental silicate rock being
501 altered, there is no constraint on how these contents may fluctuate globally during the
502 Cenozoic. Determining how each rock type (basalt, granite, shales) contribute to the global
503 weathering flux, according to change in climate, vegetation and tectonic settings is beyond the
504 capability of our simple model. This aspect is currently explored with coupled 3D-
505 climate/biogeochemical models (Taylor et al., 2012; Lefebvre et al., 2013), showing for
506 example that the position of India relative to the tropical belt strongly controls the alteration
507 of the Deccan Traps lava flows. Exploring the impact of this on the lithium cycle is a task for
508 the future.

509

510

511 **4. Conclusion**

512

513 We provide a new approach for modeling the seawater $\delta^7\text{Li}$ record, preserved in marine
514 foraminifera and carbonate records (Misra and Froelich, 2012). The Li cycle includes several
515 fluxes of importance for the carbon cycle (and hence for the climatic evolution), including
516 continental weathering and hydrothermal water-rock interactions. For this reason, we have
517 combined the C and the Li cycles, so that our proposed reconstruction of the Cenozoic Li

518 cycle is compatible with the required stability of the exospheric carbon cycle at the geological
519 timescale (Walker et al., 1981). Results are consistent with the current knowledge of the
520 behavior of Li isotopes during continental weathering: 1/ in terms of isotope fractionation
521 during dissolution and clay formation 2/in term of present-day river flux and river $\delta^7\text{Li}$.
522 In order to fit the paleovariation of the ocean $\delta^7\text{Li}$ through out the Cenozoic, the model
523 required significant Li to be stored on the continents during the Paleocene and Eocene, likely
524 in secondary phases which are Li-rich, such as phyllosilicates and oxides. Then this storage
525 flux globally decreases towards the present day, while the export to the ocean by weathering
526 increases. This storage follows indexes recording the climate evolution during the Cenozoic,
527 such as foraminifera $\delta^{18}\text{O}$ and $p\text{CO}_2$ reconstructions. This leads us to propose that climate
528 | exerted a dominant control on soil production [rates](#) during the last 70 Ma.
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675 **Table 1:** Li concentrations measured in kaolinite (Tardy et al., 1972). These clays contain
676 0.2% MgO (Tardy et al., 1972). On average, the Li level for kaolinite is estimated to be 23
677 ppm. For comparison, average Li content for smectite is found to be 27 ppm (Tardy et al.,
678 1972) and 22 ppm for granites (Teng et al., 2009).

<i>location</i>	<i>Li (ppm)</i>	<i>Reference</i>
Ivory Coast	30	Tardy et al. (1972)
	23	Tardy et al. (1972)
	53	Tardy et al. (1972)
	70	Tardy et al. (1972)
	22	Tardy et al. (1972)
	26	Tardy et al. (1972)
	4	Tardy et al. (1972)
	7	Tardy et al. (1972)
	7	Tardy et al. (1972)
	8	Tardy et al. (1972)
	32	Tardy et al. (1972)
	37	Tardy et al. (1972)
	5	Tardy et al. (1972)
35	Tardy et al. (1972)	
USA	20	Rudnick et al. 2004
Seine basin (France)	42	t.s.
Brazilian Amazon Basin	6.3	t.s
	5.3	t.s
	11.5	t.s
	11.8	t.s
Average Kaolinite	23	

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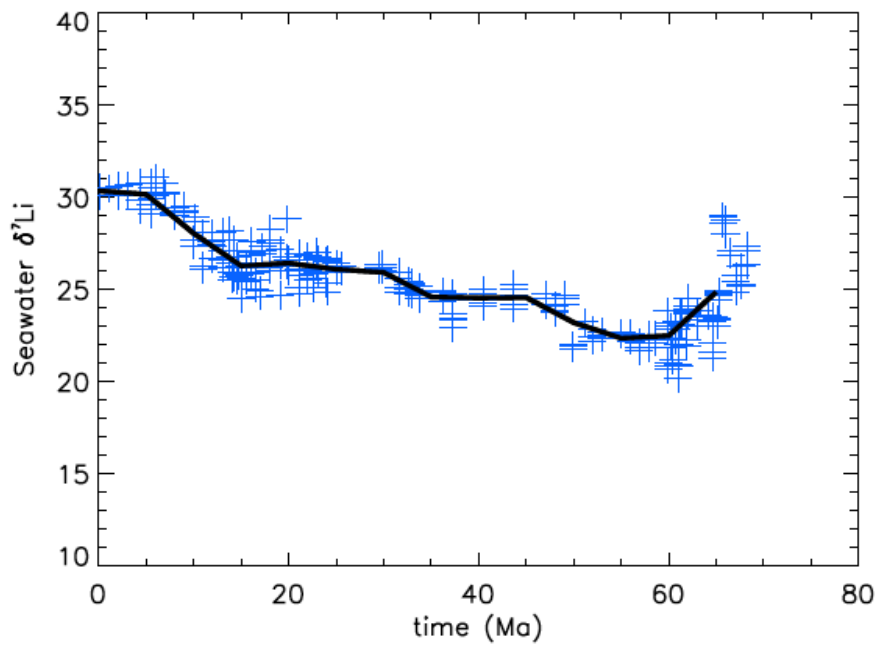
679 **Table 2:** Parameters used the model. Δ_{oc} and Δ_{land} (Li isotope fractionation during secondary
680 phase formation in the ocean and on land respectively) are chosen from within the published
681 range, such that 1/ the seawater paleo-variation exactly match the 5Myr fit of the Misra and
682 Froelich (2012) foraminifera data through the Cenozoic (0-65Ma) (shown in figure 1) and 2/
683 at time t=0 (present day), both $F_{riv}(Li)$ and δ^7Li_{riv} values must be within the published range
684 (see text for references).

	Published values	Model values
$F_{riv}(Li)$	4-12.10 ⁹ mol/yr	Free (see figures)
$F_{hyd}(Li)$	2-145.10 ⁹ mol/yr	5.10 ⁹ mol/yr
δ^7Li_{hyd}	8.5±1‰	8
δ^7Li_{UCC}	1.7±2‰	1.7
δ^7Li_{riv}	23±2‰	Fixed at 23‰ / linear / free (see figures)
Δ_{oc}	10-25‰	14‰
Δ_{land}	10-25‰	23‰
$\frac{Li}{C}_{hyd} = \frac{1}{k_2}$		6.67.10 ⁻⁴
$(\frac{Li}{(Ca+Mg)})_{UCC} = k_1$		7.5.10 ⁻³

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Figure 1

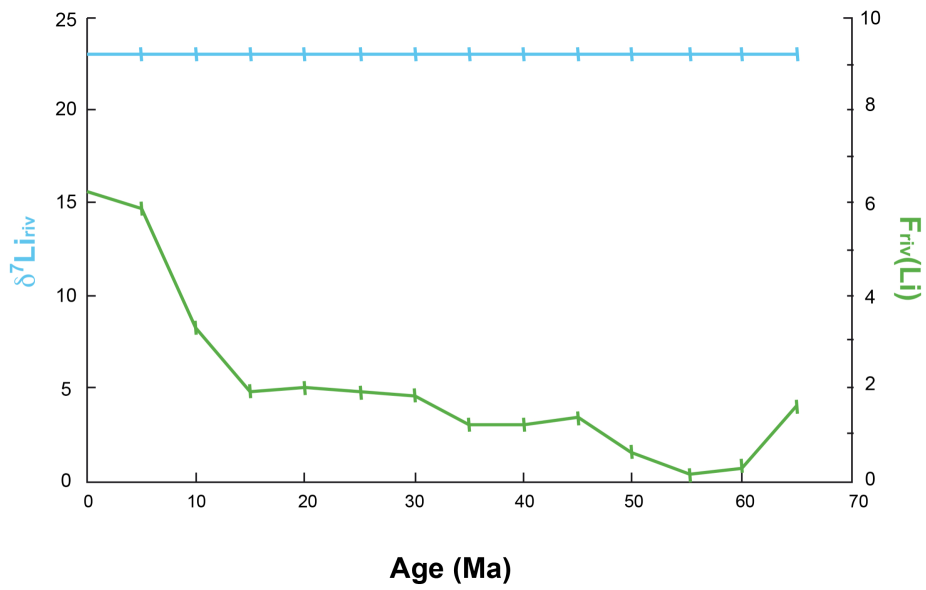


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Figure 1: Seawater $\delta^7\text{Li}$ (in ‰) as a function of time (blue symbols), modified from Misra & Froelich (2012), assuming that marine foraminifera and carbonates reflect seawater composition. The black line shows a 5Myr moving average of the data. All model simulations performed in this study are forced to exactly fit this line.

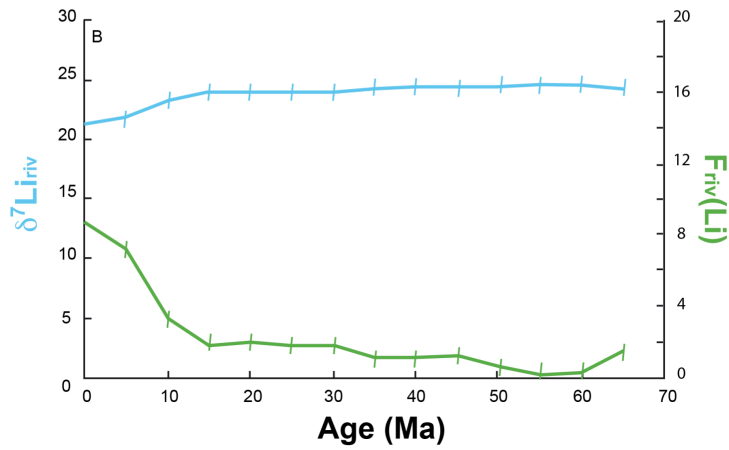
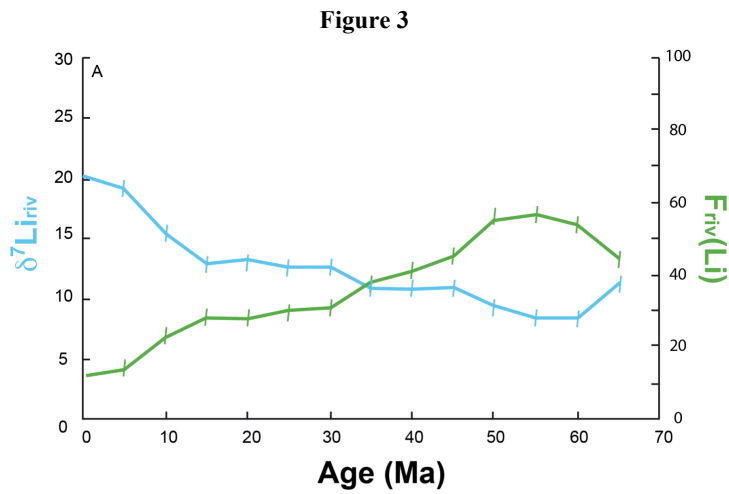
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Figure 2



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Figure 2: Simulation assuming constant $\delta^7\text{Li}_{\text{riv}}$ (in blue) as a function of time. As shown here, the seawater $\delta^7\text{Li}$ record presented in figure 1 can still be fitted if the flux of river Li (F_{riv} in 10^9 mol/yr, in green) increased significantly during the same period of time. This example demonstrates the lack of constraints on the steady-state model if only the equation for Li is considered. In addition this example shows that river $\delta^7\text{Li}$ can display temporal variations that are significantly different from the ocean $\delta^7\text{Li}$ record.



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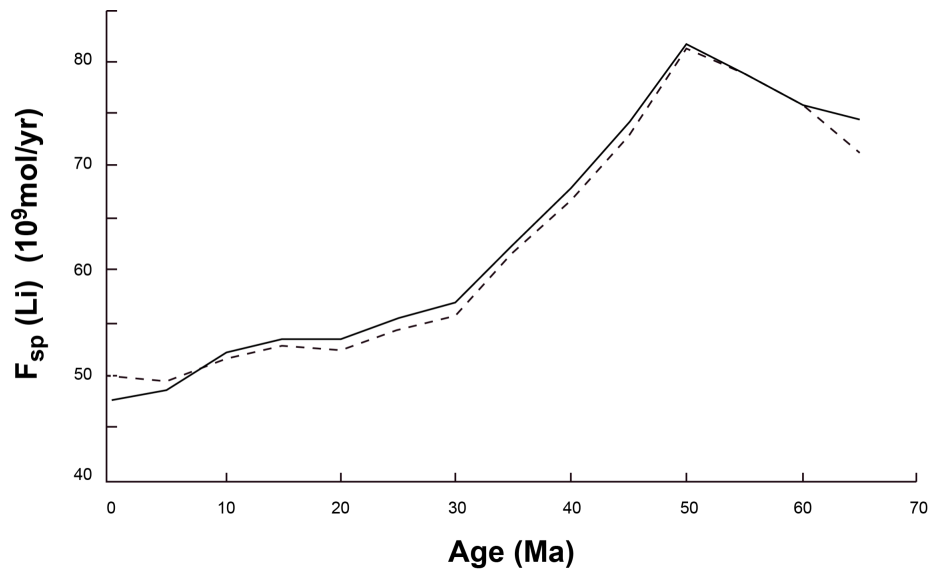
714 **Figure 3A&B:** The two solutions of the model described in the text that can both explain the
 715 seawater record (see equations 3-12, and Table 2) F_{riv} is in 10^9 mol/yr (in green). **A/** this
 716 solution is consistent with calculations performed by Misra & Froelich (2012) since low δ^7Li
 717 values are found for 60Ma rivers and then increased as a function of time (in blue) **B/** a
 718 second solution is also possible, using exactly the same set of parameters. In this case, river
 719 δ^7Li has decreased as a function of time while the Li river flux has increased.

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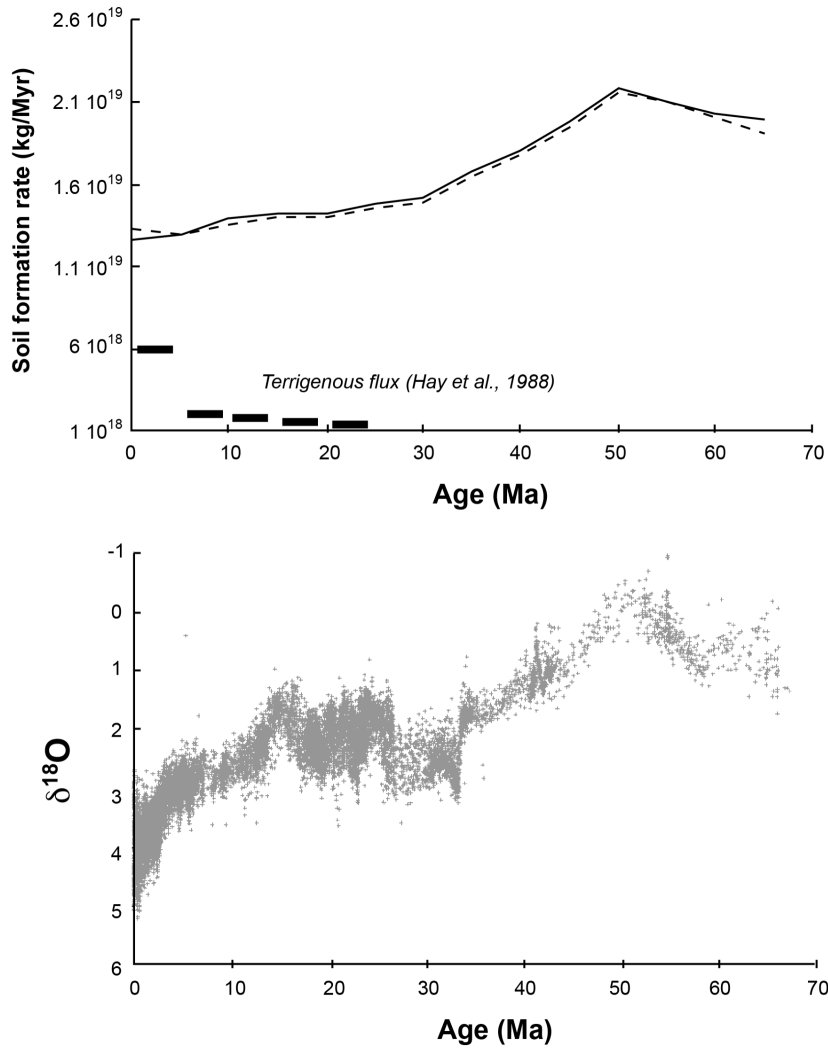
Figure 4



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Figure 4: Flux of lithium incorporated into [continental](#) secondary phases as a function of time (F_{sp} , see [equation 6](#)), following solution #2 of the modeling (shown in Figure 3B). Comparison is made using a linear evolution for river $\delta^7\text{Li}$ as a function of time, from 15‰ (at 65Ma) to 23‰ (present-day) (dashed line).

Figure 5



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735 **Figure 5:** A/ Evolution of soil formation rate as a function of time deduced from the
 736 modeling of Li data [and assuming that most secondary phases are formed in soils](#) (see text for
 737 more details). A published [estimation of evolution of terrigenous flux is shown for](#)
 738 comparison (same unit) B/ Variation of $\delta^{18}\text{O}$ of benthic foraminifera as a function of time
 739 (compilation from Zachos et al., 2001).

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