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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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Abstract

The marine record of the ocean lithium isotope composition may provide important information constraining the factors that control continental weathering and how they have varied in the past. However, the equations establishing the links between the continental flux of Li to the ocean, its Li isotope composition and the ocean Li isotope composition are under-constrained, and their resolution are related to significant uncertainties. In order to partially reduce this uncertainty, we propose a new approach that couples the C and Li cycles, such that our proposed reconstruction of the Cenozoic Li cycle is compatible with the required stability of the exospheric carbon cycle on geological timescales. The results of this exercise show, contrary to expectations, that the Li isotope composition of rivers exerts only a minor influence on the $\delta^7\text{Li}$ of the ocean. In contrast, variations in the continental flux of Li to the ocean are demonstrated to play a major role in setting the ocean $\delta^7\text{Li}$. We also provide evidence that Li storage in soils is an important element of the global Li cycle that cannot be neglected during the Cenozoic. Our modeling of the published foraminifera record highlight a close link between soil formation rate and indexes recording the climate evolution during the Cenozoic, such as foraminifera $\delta^{18}\text{O}$ and $p\text{CO}_2$ reconstructions. This leads us to propose that climate exerted a dominant control on soil production and therefore on continental weathering during the last 70 Ma.

1 Introduction

Weathering (chemical erosion) of continental Ca-Mg rich silicates serves as a major sink of atmospheric CO_2 . However, determining how such weathering has evolved in the past, as a function of climate or tectonic activity, remains a challenge. Filling this gap in our knowledge is essential if we are to understand how global temperature is regulated on geological timescales. The great potential of lithium isotopes to trace alteration processes has recently been highlighted (see e.g. review in Burton and Vigier, 2011).

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Nevertheless, analytical difficulties have limited their use as a marine paleoproxy. Misra and Froelich (2012) determined the evolution of the lithium isotopic composition of bulk carbonates and planktonic foraminifera over the past 68 Ma. These authors argue that this record reflects ocean-wide variations, and that the 9‰ increase of the marine $\delta^7\text{Li}$ from the Paleocene to the present (see Fig. 1), can be explained by an increase of river $\delta^7\text{Li}$ from 3‰ 60 Ma ago, to 23‰ at present. To account for such a dramatic change in riverine $\delta^7\text{Li}$ Misra and Froelich (2012) invoke a change of the alteration regime (from a congruent to a weathering-limited regime) and an increase of clay formation (which fractionates Li isotopes) in mountainous – rapidly eroding – areas. This assertion links the secular increase in the marine $\delta^7\text{Li}$ record to increasing tectonic uplift and mountain building over the course of the Cenozoic. Under this interpretive framework, continental weathering during the early Paleogene (≈ 60 Myr ago) was characterized principally by high dissolution rates of continental rocks and relatively low rates of clay formation and transport. Such a weathering regime offers a mechanism for producing low $\delta^7\text{Li}$ values in rivers, close to that of the continental crust, because dissolution is not accompanied by significant Li isotope fractionation. Later in the Cenozoic, as tectonic activity intensifies, incongruent weathering and clay formation is supposed to become more significant, leading to a shift to larger riverine $\delta^7\text{Li}$.

However, several lines of evidence call this interpretation of the seawater record into question, and in particular the notion that low $\delta^7\text{Li}$ values in rivers of the Cretaceous could be sustained by predominately congruent weathering. Indeed, a congruency of the weathering process, that would correspond to small rates of clay formation or soil production, at 60 Ma is not supported by the occurrence of thick weathering profiles found at this period of time (e.g. Beauvais and Chardon, 2013; Tavlan et al., 2011; Meshram and Randiv, 2011). A compilation of about 80 ODP or DSDP core sites indicate that the deep seawater during the Paleocene exhibited low $\delta^{18}\text{O}$ values, with benthic foraminifera $\delta^{18}\text{O}$ values between 3 and 4‰ lower than at present (Zachos et al., 2001). This feature is interpreted as much warmer climatic conditions, in agreement with recent reconstructions of atmospheric $p\text{CO}_2$ at 60 Ma, ranging between 400

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and 1000 ppmv (Beerling and Royer, 2011). These conditions have favored the formation of thick weathering profiles, in particular of lateritic regolith mantles rich in kaolinite and/or bauxite. These resistant phases are depleted in major cations playing a key role in the carbon cycle (such as Ca and Mg), but they contain significant amounts of Li. Our compilation of Li levels in kaolinite-rich samples (Table 1) shows that they are – on average – similar to the Li content estimated for the continental crust granites (22 ppm \pm 4 ppm, Teng et al., 2009). They may therefore have played a key role in the continental Li cycle. Li-containing regoliths provide empirical evidence against the idea that congruent weathering prevails during warm intervals of Earth history driving riverine $\delta^7\text{Li}$ to values similar to average upper crust.

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

Our model takes into account the changes in Li flux coming from the continents in response to a balance between (1) dissolution rates of continental rocks releasing Li in waters and (2) temporary storage of Li into secondary phases formed in weathering profiles. Since lithium isotopes fractionate during clay mineral accumulation (e.g. Huh et al., 2001; Kisakurek et al., 2004; Rudnick et al., 2004), soil formation rate is expected to drive the Li isotope composition of rivers. One illustration is that, at present, the mean $\delta^7\text{Li}$ value of the continental runoff (+23‰; Huh et al., 1998) is much higher than the average $\delta^7\text{Li}$ value estimated for the continental crust granites (+2 \pm 4‰, Teng et al., 2009). Since Li isotopes do not fractionate during dissolution, this difference is best explained by isotope fractionation during the formation of secondary phases (Vigier et al., 2009; von Strandmann et al., 2010; Bouchez et al., 2013). Consequently, at present, at the world-wide scale, a significant part of the Li released by continental dissolution is stored in ^6Li -rich soils, resulting in heavy signatures (^7Li -rich) in rivers. Experimental in-

vestigations, as well as soil studies support these findings (e.g. Wimpenny et al., 2010; Vigier et al., 2008; Lemarchand et al., 2010). Thus, we explore how Li storage in soils at the global scale has affected the ocean $\delta^7\text{Li}$ value, as well as the potential of ocean $\delta^7\text{Li}$ to quantify the balance between physical denudation and chemical alteration and its variation throughout the Cenozoic.

2 Model equations and basics

2.1 Seawater isotopic balance

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

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

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 hydrothermal fluids respectively. Δ_{oc} represents the absolute value of the fractionation factor of the Li isotopes during marine secondary phase formation. In literature, this factor ranges between -10 and -25% depending on the temperature at which authigenic phases are being formed (Chan et al., 1992, 1993; Vigier et al., 2008).

The residence time of Li in the ocean is equal to 1 million years. Given that we are exploring the time evolution of its isotopic cycle over the whole Cenozoic (10^7 year timescale), we can assume steady-state for both the elemental (i.e. all the Li carried by rivers and released by hydrothermal activity into the ocean is removed through authi-

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genic clay formation: $F_{riv} + F_{hyd} = F_{clay}$) and isotopic Li cycles. Equation (1) becomes:

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

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

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

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

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

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shows that, by taking into account the Li ocean budget only, the system of equations is under-constrained and it is not possible to calculate the temporal variations of riverine $\delta^7\text{Li}$ without making assumptions about the link between $F_{\text{riv}}^{\text{Li}}$ and δ_{riv} . It also shows that low seawater $\delta^7\text{Li}$, as highlighted by early Eocene foraminifera can be compatible with a high $\delta^7\text{Li}$ value of the riverine flux. Our result shows therefore that low $\delta^7\text{Li}$ in the ocean does not systematically imply low river $\delta^7\text{Li}$. The temporal variations of the riverine Li flux also need to be established. In the following, we add constraints on this aspect and the Li cycle, by coupling it to the carbon cycle.

2.2 Walker paleothermostat

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

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

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

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

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

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In contrast with hydrothermal conditions, Li is much less “mobile” on the continents, as reflected by low Li contents in river waters (ppb level) while granites (the main source of river Li) are enriched in Li compared to oceanic crust. Indeed, first, thermodynamic laws indicate that dissolution rate is lower at lower temperature. Additionally, it is observed that most of the Li carried by rivers to the ocean is mainly located in the particulate load (> 70 %, e.g. Millot et al., 2010), while the dissolved Li represents only a minor proportion. This is consistent with the fact that Li can be significantly incorporated into the structure of secondary minerals, mainly clays. As a consequence, the flux of dissolved Li carried by rivers may not be proportional to the flux of CO₂ consumed during the leaching or dissolution of continental mineral phases. The relationship linking the flux of lithium carried by rivers and the flux of atmospheric CO₂ consumed by mineral dissolution becomes:

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

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

If present-day conditions might reflect a recent disequilibrium due to the last glaciation (Vance et al., 2009), at the Cenozoic timescale, formation of thick weathering profiles with significant residence time (> 0.5 Ma) are likely to have impacted the Li cycle. We assume that most of secondary phases present in these profiles are largely depleted in cations, in particular in Ca and Mg, and therefore do not affect significantly the carbon budget.

Combining Eqs. (4)–(6) we obtain the following relationship:

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

where the flux of riverine Li is a function of both the hydrothermal flux and of the soil formation rate on the continents.

2.3 Riverine $\delta^7\text{Li}$

All published studies indicate the existence of a strong isotope fractionation during the formation of secondary phases, such as clays or Fe oxides, always in favor of the light isotope (^6Li). At periods when the soil production and thickness increased in the past, we therefore expect that the $\delta^7\text{Li}$ of river waters increase, since more ^6Li is incorporated and stored into soils. In fact, the riverine $\delta^7\text{Li}$ is the result of the competition (e.g. Bouchez et al., 2013) between the isotopically congruent dissolution of fresh bedrock, and the precipitation of secondary phases with an isotope fractionation Δ_{land} (Table 2), such that:

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

with δ_{UCC} being the average $\delta^7\text{Li}$ value estimated for the upper continental crust (Table 2).

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

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

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} . To date the published values of $\delta^7\text{Li}$ of most rivers (e.g. Huh et al., 1998; Millot et al., 2010; Kisakurek et al., 2004) are significantly greater than the $\delta^7\text{Li}$ estimated for UCC (2‰, Teng et al., 2009), and thus are consistent with Eq. (9).

2.4 Method for solving the model

We assume that the foraminifera $\delta^7\text{Li}$ reflect the ocean $\delta^7\text{Li}$, as assumed in Misra and Froelich (2012) and in Hathorne and James (2006). We consider that potential vital effects, responsible for changes of Li isotope fractionation during foraminifera growth may explain some observed rapid (< 0.5 Ma) changes of foraminifera Li isotope compositions, but we do not take into account these effects since the model aims at working at the multi million scale only. A moving average of the oceanic lithium isotopic data is calculated, with a window width of 5 millions of years (see Fig. 1). This data smoothing ensure the validity of the steady-state hypothesis and remove all short term fluctuations potentially related to vital effects.

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

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

where A_1 and A_2 are equal to :

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

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

The values for the various parameters used in the model are described in Table 2. As long as the discriminant of Eq. (10) is strictly positive, Eq. (10) has two solutions for $F_{\text{riv}}^{\text{Li}}$. This means that two radically different histories of $F_{\text{riv}}^{\text{Li}}$ can explain the rise of the Li isotopic composition of seawater.

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soil Li storage was high from 65 to 50 Myr, and then decreased continuously until its stabilization at about 20 Myr ago (Fig. 4).

In order to be more quantitative, check the consistency of these results and compare them to other proxies, we estimated the corresponding soil formation rates, assuming a Li concentration of 25 ppm, which corresponds to an average soil Li concentration, including data shown in Table 1. This value may be associated with a large error, as there are currently only few soil data. It may also have varied as a function of time, although this is not supported by the relative narrow range of Li concentration of the most abundant clays. Nevertheless, this assumption allows us to assess if the order of magnitude for fluxes extracted from our model makes sense. Also, a compilation of Li contents for the most abundant low-T continental clays show that the average Li value is not so different from one type of clay to another (Tardy et al., 1972; Table 1). During the Cenozoic, we thus estimate that soil formation rate ranged from $2.2 \times 10^{19} \text{ kg Ma}^{-1}$ to a present-day value of $1.3 \times 10^{19} \text{ kg Ma}^{-1}$, i.e. $2.2 \times 10^{10} \text{ tyr}^{-1}$ to $1.3 \times 10^{10} \text{ tyr}^{-1}$. For comparison, Syvitski et al. (2003) estimated a present-day global physical denudation rate of $2 \times 10^{10} \text{ tyr}^{-1}$. Reconstitution of paleo-denudation rate during the Cenozoic are controversial (e.g. Willenbring and von Blanckenburg, 2010), but given the uncertainties typical of global scale estimations, it is worth noting that the calculated soil formation falls quite close (less than an order of magnitude difference) to the global denudation estimate, indicating that our calculations – based on C and Li cycles and published values for corresponding parameters – make sense.

3.2 Assessing the role of climate

Except for the last few Ma, the paleo-reconstruction of soil formation rate during the Cenozoic is remarkably parallel to the $\delta^{18}\text{O}$ values measured in benthic foraminifera (Zachos et al., 2001, see Fig. 5b). This strongly suggests a major role of climate on continental weathering, and more particularly on the soil development at the global scale. When the climate gets cooler, soil formation rates decrease. A potential increase of weathering rates due to orogenesis and mountain building during the Cenozoic is

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therefore not able to compensate the role of temperature. In the open debate concerning the controls of continental chemical erosion rates at global scale over the Cenozoic, Li isotopes yield good evidence of the predominance of climate over mechanical erosion. Specifically the fact that soil formation rates predicted by the model parallel the global benthic oxygen isotope record shows that the impact of orogenesis is not strong enough to counter-balance the impact of temperature decrease.

More closely inspecting the comparison between soil formation rate, $\delta^{18}\text{O}$ and $p\text{CO}_2$ paleo-variations reveals four remarkable features:

1. High soil formation rates during the Paleocene and Early Eocene, coincides with high $p\text{CO}_2$ estimations (Beerling and Royer, 2011) as well as low foraminifera $\delta^{18}\text{O}$ values. This strongly suggests that weathering rates were high because of climatic conditions favoring both dissolution of silicate rocks and formation of secondary minerals and laterites.
2. A sharp decrease of soil formation rate coeval with a sharp increase in foraminifera $\delta^{18}\text{O}$ during the Eocene until the beginning of the Oligocene. This co-variation suggests a predominant role of climate cooling on continental soil production. However, during this period of time, we cannot exclude a global thinning of soils by mountain building and orogenesis. Steeper slopes, higher relief, and increasing impact of landslide contribute significantly to reduce the world average soil thickness.
3. A stabilization of the weathering rates between 30 and 10 Ma, which matches the plateaus exhibited by $p\text{CO}_2$ (not shown here, but see Beerling and Royer, 2011) and $\delta^{18}\text{O}$ proxies.
4. A decoupling between soil formation rate, benthic foraminifera $\delta^{18}\text{O}$ and physical denudation rate during the Quaternary period. Indeed, both soil formation rates and $p\text{CO}_2$ estimates remain globally stable during this period. However, foraminifera $\delta^{18}\text{O}$ and denudation rates (e.g. Hay et al., 1988) show significant

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Table 1. Li concentrations measured in kaolinite (Tardy et al., 1972). These clays contain 0.2 % MgO (Tardy et al., 1972). On average, the Li level for kaolinite is estimated to be 23 ppm. For comparison, average Li content for smectite is found to be 27 ppm (Tardy et al., 1972) and 22 ppm for granites (Teng et al., 2009).

location	Li (ppm)	Reference
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)
USA	5	Tardy et al. (1972)
	35	Tardy et al. (1972)
USA Seine Basin (France)	20	Rudnick et al., 2004
	42	t.s.
Brasilian 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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Table 2. Parameters used in the model. Δ_{oc} and Δ_{land} (Li isotope fractionation during secondary phase formation in the ocean and on land respectively) are chosen from within the published range, such that (1) the seawater paleo-variation exactly match the 5 Myr fit of the Misra and Froelich (2012) foraminifera data through the Cenozoic (0–65 Ma) (shown in Fig. 1) and (2) at time $t = 0$ (present day), both $F_{\text{riv}}(\text{Li})$ and $\delta^7\text{Li}_{\text{riv}}$ values must be within the published range (see text for references).

	Published values	Model values
$F_{\text{riv}}(\text{Li})$	$4\text{--}12 \times 10^9 \text{ mol yr}^{-1}$	Free (see figures)
$F_{\text{hyd}}(\text{Li})$	$2\text{--}145 \times 10^9 \text{ mol yr}^{-1}$	$5 \times 10^9 \text{ mol yr}^{-1}$
$\delta^7\text{Li}_{\text{hyd}}$	$8.5 \pm 1 \text{ ‰}$	8
$\delta^7\text{Li}_{\text{UCC}}$	$1.7 \pm 2 \text{ ‰}$	1.7
$\delta^7\text{Li}_{\text{riv}}$	$23 \pm 2 \text{ ‰}$	Fixed at 23 ‰ / linear / free (see figures)
Δ_{oc}	10–25 ‰	14 ‰
Δ_{land}	10–25 ‰	23 ‰
$C/\text{Li}_{\text{hyd}} = k_2$		6.67×10^{-4}
$(\text{Li}/(\text{Ca} + \text{Mg}))_{\text{UCC}} = k_1$		7.5×10^{-3}

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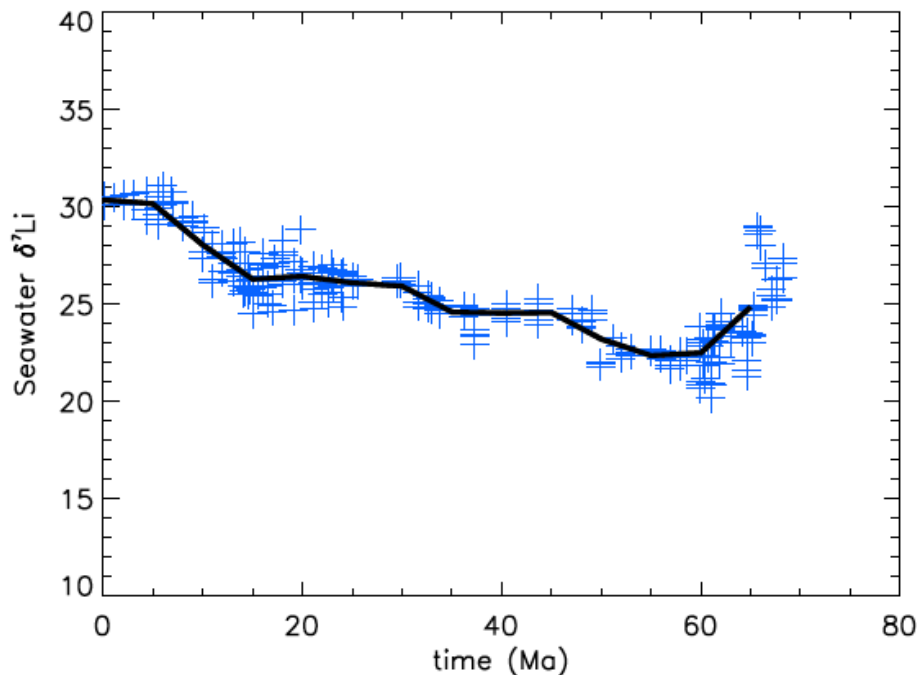


Figure 1. Seawater $\delta^7\text{Li}$ (in ‰) as a function of time (blue symbols), modified from Misra and Froelich (2012), assuming that marine foraminifera and carbonates reflect seawater composition. The black line shows a 5 Myr moving average of the data. All model simulations performed in this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

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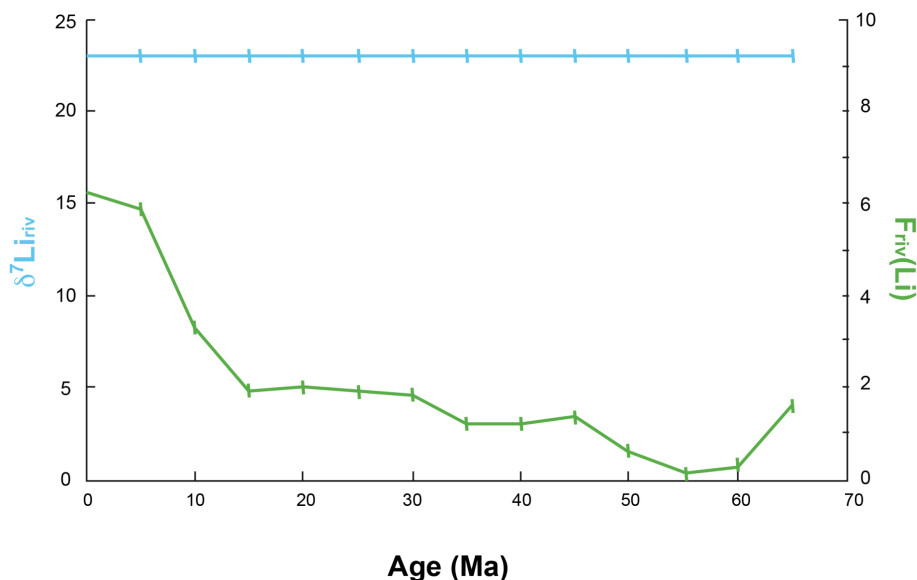


Figure 2. Simulation assuming constant $\delta^7\text{Li}_{\text{riv}}$ (in blue) as a function of time. As shown here, the seawater $\delta^7\text{Li}$ record presented in Fig. 1 can still be fitted if the flux of river Li (F_{riv} in 10^9 mol yr^{-1} , in green) increased significantly during the same 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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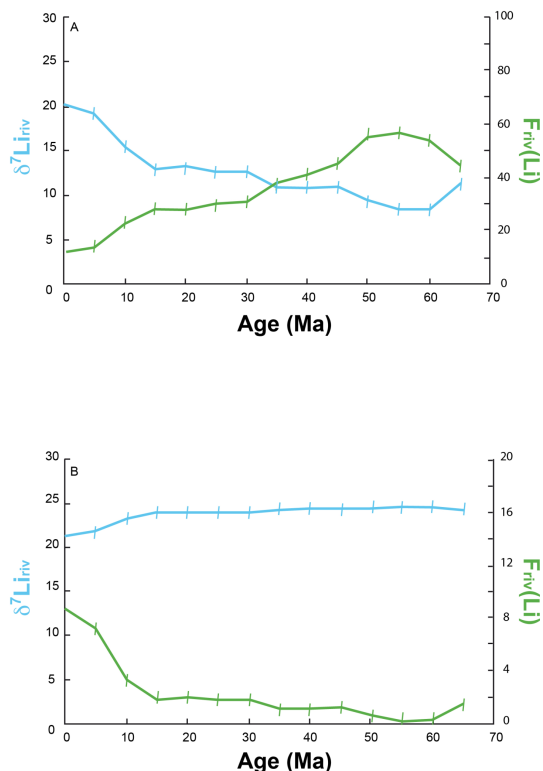


Figure 3. The two solutions of the model described in the text that can both explain the sea-water record (see Eqs. 3–12, and Table 2) F_{riv} is in 10^9 mol yr^{-1} (in green). **(A)** this solution is consistent with calculations performed by Misra and Froelich (2012) since low $\delta^7\text{Li}$ values are found for 60 Ma rivers and then increased as a function of time (in blue) **(B)** a second solution is also possible, using exactly the same set of parameters. In this case, river $\delta^7\text{Li}$ has decreased as a function of time while the Li river flux has increased.

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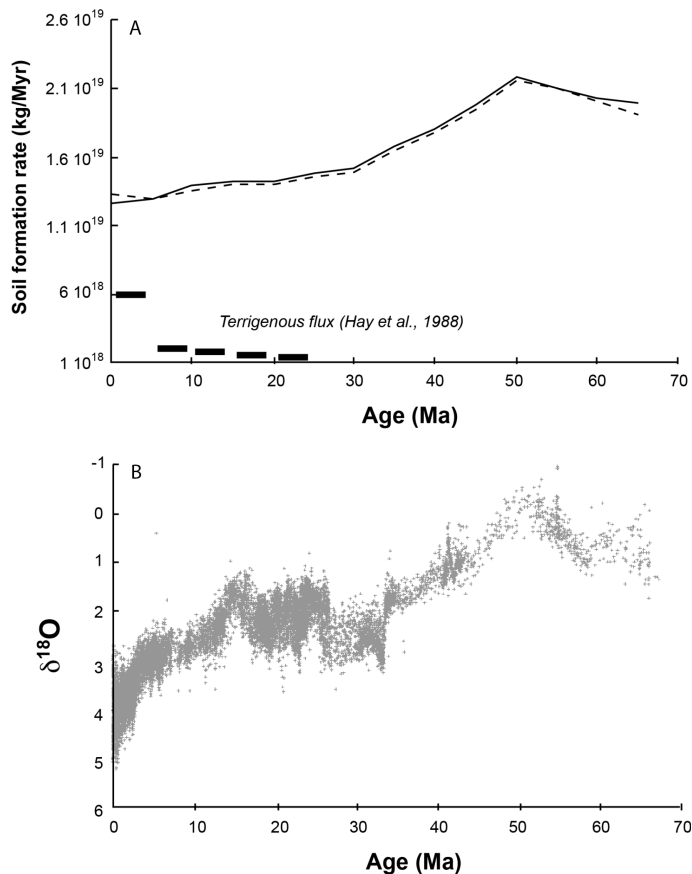


Figure 5. (A) Evolution of soil formation rate as a function of time deduced from the modeling of Li data (see text for more details). A published stimulation of evolution of terrigenous flux is shown for comparison (same unit). (B) Variation of $\delta^{18}\text{O}$ (in ‰) of benthic foraminifera as a function of time (compilation from Zachos et al., 2001).