

This discussion paper is/has been under review for the journal Climate of the Past (CP).
Please refer to the corresponding final paper in CP if available.

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

N. Vigier¹ and Y. Godderis²

¹Laboratoire d'Océanographie de Villefranche-sur-Mer, CNRS, UPMC, 06230 Villefranche-sur-Mer, France

²Géosciences Environnement Toulouse, CNRS, Université Paul Sabatier, 31400 Toulouse, France

Received: 9 June 2014 – Accepted: 16 July 2014 – Published: 28 July 2014

Correspondence to: N. Vigier (nathalie.vigier@obs-vlfr.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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).

CPD

10, 3027–3051, 2014

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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

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-

CPD

10, 3027–3051, 2014

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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).

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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.

CPD

10, 3027–3051, 2014

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3 Results and discussion

3.1 Paleo-variations of continental weathering

Two solutions have thus been found for the Cenozoic (represented in Fig. 3a and b). The first solution (Fig. 3a) implies an increase of the riverine $\delta^7\text{Li}$ over the Cenozoic, associated to a decrease of riverine Li flux with time. We consider this scenario as the less robust of the two possible solutions because it is inconsistent with geological and mineralogical evidence which are based on (1) high Li content in laterites rich in kaolinite such as those observed in the Paleocene (Table 1), and that would lead to low Li flux in rivers, and (2) a decrease of the river Li flux towards recent time that is difficult to reconcile with the Sr/Ca, $^{87}\text{Sr}/^{86}\text{Sr}$ and the $^{187}\text{Os}/^{188}\text{Os}$ ocean curves (e.g. Lear et al., 2003; Li and Elderfield, 2013). This first solution is close to the scenario described in details by Misra and Froelich (2012), arguing for an increasing contribution of orogenesis on silicate dissolution, clay formation and CO_2 consumption towards recent time. In this scenario, sequestration of lithium in clays increased from the past towards the present day.

Surprisingly, our model results demonstrate that a second scenario that is more consistent with geological and isotope observations, can also explain the Cenozoic Li isotope record. Indeed, Fig. 3b shows that the $\delta^7\text{Li}$ paleorecord mainly reflects an increase of the riverine Li flux through the Cenozoic. As illustrated in Fig. 4, this increase is not due to an increase in the dissolution rate of the silicate lithologies, but is mostly due to the decrease of Li storage in soils. In order to test the robustness of this result, we performed two different simulations, using (1) the whole set of equations (for both C and Li, see Sect. 2), and (2) an imposed variation of δ_{riv} that is arbitrarily forced to increase linearly from 15‰ at 65 Ma to 23‰, its present day value (in that case, only the Li budget is solved, not C). Both simulations lead to similar trends, where Li_{soil} decrease as a function of time (see Fig. 4). This strongly suggests the robustness of the observed decrease, and also confirms that the Li isotope composition of rivers plays only a minor role in the ocean isotopic variation. Overall, these results show that

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

CPD

10, 3027–3051, 2014

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

- Beauvais, A. and Chardon, D.: Modes tempo, and spatial variability of Cenozoic cratonic denudation: the West African example, *Geochem. Geophys. Geos.*, 14, 1590–1608, doi:10.1002/ggge.20093, 2013.
- 5 Beerling D. J. and Royer, D. R.: Convergent cenozoic CO₂ history, *Nat. Geosci.*, 4, 418–420, doi:10.1038/ngeo1186, 2011.
- Berner, R. A.: *The Phanerozoic Carbon Cycle: CO₂ and O₂*, Oxford University Press, 160 pp., 2004.
- Bouchez, J., Von Blanckenburg, F., and Schuessler, J. A.: Modeling novel stable isotope ratios in the weathering zone, *Am. J. Sci.*, 313, 267–308, doi:10.2475/04.2013.01, 2013.
- 10 Burton, K. W. and Vigier, N.: Lithium isotopes as tracers in marine and terrestrial environments, in: *Handbook of Environmental Isotope Geochemistry*, 41–61, 2011.
- Chan, L.-H., Edmond, J. M., Thompson, G., and Gillis, K.: Lithium isotopic composition of submarine basalts: implications for the lithium cycle to the ocean, *Earth Planet. Sc. Lett.*, 108, 151–160, 1992.
- 15 Chan, L.-H., Edmond, J. M., and Thompson, G.: A lithium isotope study of hot springs and metabasalts from mid ocean ridge hydrothermal systems, *J. Geophys. Res.*, 98, 9653–9659, 1993.
- Chan, L.-H., Gieskes, J. M., You, C.-F., and Edmond, J. M.: Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas Basin, Gulf of California, *Geochim. Cosmochim. Ac.*, 58, 4443–4454, 1994.
- 20 Chan, L.-H., Leeman, W. P., and Plank, T.: Lithium isotopic composition of marine sediments, *Geochem. Geophys. Geos.*, 7, Q06005, doi:10.1029/2005GC001202, 2006.
- Engebretson, D. C., Kelley, K. P., Cashman, H. J., and Richard, M. A.: 180 million years of subduction, *GSA Today*, 2, 93–100, 1992.
- 25 Godderis, Y. and Francois, L. M.: The Cenozoic evolution of the strontium and carbon cycles: relative importance of continental erosion and mantle exchanges, *Chem. Geol.*, 126, 169–190, 1995.
- Foustoukos, D. I., James, R. H., Berndt, M. E., and Seyfried Jr., W. E.: Lithium isotopic systematic of hydrothermal vent fluids at the Main Endeavour Field, Northern Juan de Fuca Ridge, *Chem. Geol.*, 212, 17–26, 2004.
- 30

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

- Hathorne, E. C. and James, R. H.: Temporal record of lithium in seawater: a tracer for silicate weathering?, *Earth Planet. Sc. Lett.*, 246, 393–406, 2006.
- Hay, W. W., Sloan, J. L. I., and Wold, C. N.: The mass/age distribution of sediments on the ocean floor and the global rate of loss of sediment, *J. Geophys. Res.*, 93, 14933–14940, 1988.
- 5 Huh, Y., Chan, L.-H., Zhang, L., and Edmond, J. M.: Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget, *Geochim. Cosmochim. Ac.*, 62, 2039–2051, 1998.
- Huh, Y., Chan, L.-H., and Edmond, J. M.: Lithium isotopes as a probe of weathering processes: Orinoco River, *Earth Planet. Sc. Lett.*, 194, 189–199, 2001.
- 10 Kisakurek, B., Widdowson, M., and James, R. H.: Behaviour of Li isotopes during continental weathering: the Bidar laterite profile, India, *Chem. Geol.*, 212, 27–44, 2004.
- Kump, L. R. and Arthur, M. A.: Global chemical erosion during the Cenozoic: weatherability balances the budgets, in: *Tectonics Uplift and Climate Change*, edited by: Ruddiman, W., Plenum Press, NY, 399–426, 1997.
- 15 Lear, C. H., Elderfield, H., and Wilson, P. A.: A Cenozoic seawater Sr/Ca record from benthic foraminiferal calcite and its application in determining global weathering fluxes, *Earth Planet. Sc. Lett.*, 208, 69–84, 2003.
- Lefebvre, V., Donnadieu, Y., Godd ris, Y., Fluteau, F., and Hubert-Th ou, L.: Was the Antarctic glaciation delayed by a high degassing rate during the early Cenozoic?, *Earth Planet. Sc. Lett.*, 371, 203–211, 2013.
- 20 Lemarchand, E., Chabaux, F., Vigier, N., Millot, R., and Pierret, M.-C.: Lithium isotope systematics in a forested granitic catchment (Strengbach, Vosges Mountains, France), *Geochim. Cosmochim. Ac.*, 74, 4612–4628, 2010.
- Li, G. and Elderfield, H.: Evolution of carbon cycle over the past 100 million yr, *Geochim. Cosmochim. Ac.*, 103, 11–25, 2013.
- 25 Meshram, R. R. and Randive, K. R.: Geochemical study of laterites of the Jamnagar district, Gujarat, India: implications on parent rock, mineralogy and tectonics, *J. Asian Earth Sci.*, 42, 1271–1287, doi:10.1016/j.jseaes.2011.07.014, 2011.
- 30 Millot, R., Vigier, N., and Gaillardet, J.: Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada, *Geochim. Cosmochim. Ac.*, 74, 3897–3912, 2010.
- Misra, S. and Froelich, P. N.: Lithium isotope history of cenozoic seawater: changes in silicate weathering and reverse weathering, *Science*, 335, 818–823, 2012.

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Mottl, M. J., Seewald, J. S., Wheat, C. J., Tivey, M. K., Michael, P. J., Proskurowski, G., McCollom, T. M., Reeves, E., Sharkey, J., You, C. F., Chan, L. H., and Pichler, T.: Chemistry of hot springs along the Eastern Lau Spreading Center, *Geochim. Cosmochim. Ac.*, 75, 1013–1038, 2011.
- 5 Rudnick, R. L., Tomascak, P. B., Njoa, H. B., and Gardnerb, L. R.: Extreme lithium isotopic fractionation during continental weathering revealed in saprolites from South Carolina, *Chem. Geol.*, 212, 45–57, 2004.
- von Strandmann, P. A. E. P., Burton, K. W., James, R. H., van Calsteren, P., and Gislason, S. R.: Assessing the role of climate on uranium and lithium isotope behaviour in rivers draining a basaltic terrain, *Chem. Geol.*, 270, 227–239, 2010.
- 10 Syvitskia, J. P. M., Peckhama, S. D., Hilbermana, R., and Mulder, T.: Predicting the terrestrial flux of sediment to the global ocean: a planetary perspective, *Sediment. Geol.*, 162, 5–24, 2003.
- Tardy, Y., Krempp, G., and Trauth, N.: Le lithium dans les minéraux argileux des ciments et des sols, *Geochim. Cosmochim. Ac.*, 36, 397–412, 1972.
- 15 Tavlan, M., Thorne, R., and Herrington, R. J.: Uplift and lateritization history of the Caldag ophiolite in the context of Neo-Tethyan ophiolite obduction and uplift: implications for the Cenozoic weathering history of western Anatolia, *J. Geol. Soc. London*, 168, 927–940, 2011.
- Teng, F.-Z., Rudnick, R. L., McDonough, W. F., and Wu, F. Y.: Lithium isotopic systematics of A-type granites and their mafic enclaves: further constraints on the Li isotopic composition of the continental crust, *Chem. Geol.*, 262, 370–379, 2009.
- 20 Tomascak, P. B.: Developments in the understanding and application of lithium isotopes in the Earth and Planetary Sciences, *Rev. Mineral. Geochem.*, 55, 153–195, 2004.
- Vance, D., Teagle, D. A. H., and Foster, G. L.: Variable Quaternary chemical weathering rates and imbalances in marine geochemical budgets, *Nature*, 458, 493–496, 2009.
- 25 Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S., and France-Lanord, C.: Quantifying Li isotope fractionation during smectite formation and implications for the Li cycle, *Geochim. Cosmochim. Ac.*, 72, 780–792, 2008.
- Vigier, N., Gislason, S. R., Burton, K. W., Millot, R., and Mokadem, F.: The relationship between riverine lithium isotope composition and silicate weathering rates in Iceland, *Earth Planet. Sc. Lett.*, 287, 434–441, 2009.
- 30

Walker, J. C. G., Haysand, P. B., and Kasting, J. F.: A negative feedback mechanism for the long-term stabilization of Earth's surface temperature, *J. Geophys. Res.*, 86, 9776–9782, 1981.

Willenbring, J. K. and von Blanckenburg, F.: Long-term stability of global erosion rates and weathering during late-Cenozoic cooling, *Nature*, 465, 211–214, 2010.

Wimpenny, J., Gíslason, S. R., James, R. H., Gannoun, A., Von Strandmann, P., and Burton, K. W.: The behaviour of Li and Mg isotopes during primary phase dissolution and secondary mineral formation in basalt, *Geochim. Cosmochim. Ac.*, 74, 5259–5279, 2010.

Zachos, J. C., Shackleton, N. J., Revenaugh, J. S., Pälike, H., and Flower, B. P.: Climate response to orbital forcing across the Oligocene–Miocene boundary, *Science*, 292, 274–277, 2001.

CPD

10, 3027–3051, 2014

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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)
	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	

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

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}

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

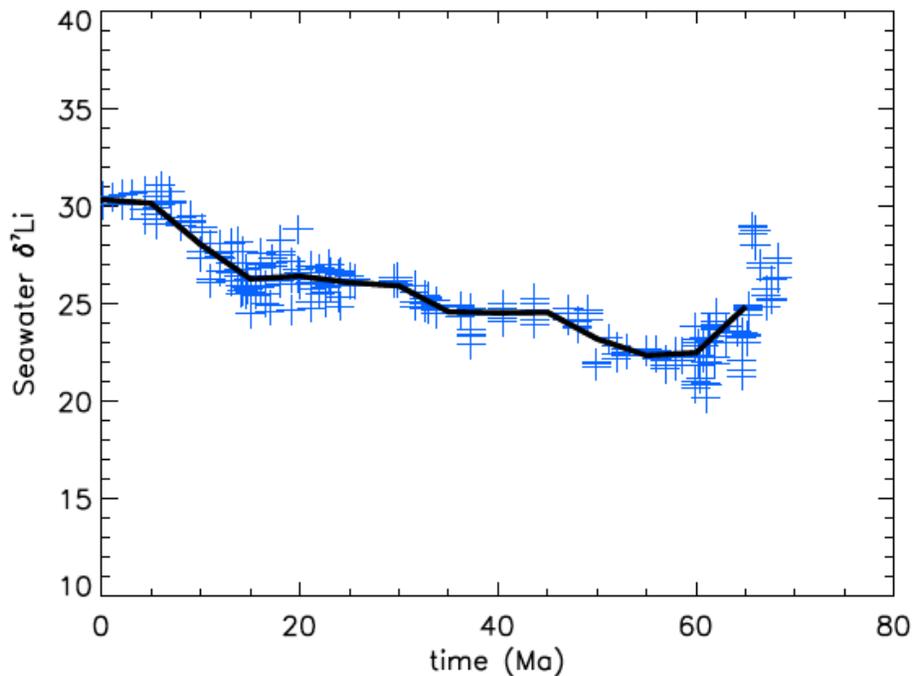


Figure 1. Seawater $\delta^7\text{Li}$ (in ‰) as a function of time (blue symbols), modified from Misra and Froelich (2012), assuming that marine foraminifera and carbonates reflect seawater composition. The black line shows a 5 Myr moving average of the data. All model simulations performed in this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

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

[Title Page](#)

[Abstract](#) [Introduction](#)

[Conclusions](#) [References](#)

[Tables](#) [Figures](#)

[◀](#) [▶](#)

[◀](#) [▶](#)

[Back](#) [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

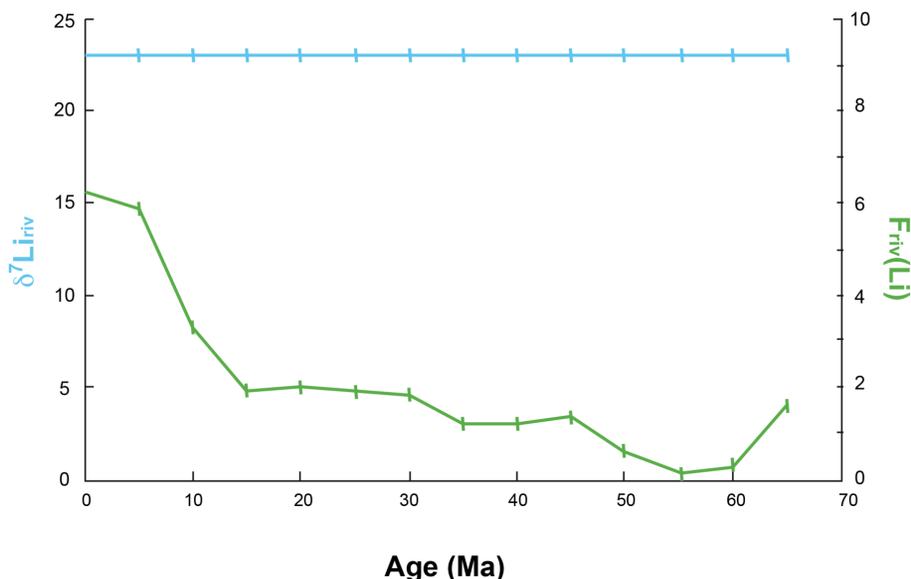


Figure 2. Simulation assuming constant $\delta^7\text{Li}_{\text{riv}}$ (in blue) as a function of time. As shown here, the seawater $\delta^7\text{Li}$ record presented in Fig. 1 can still be fitted if the flux of river Li (F_{riv} in 10^9 mol yr^{-1} , in green) increased significantly during the same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

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

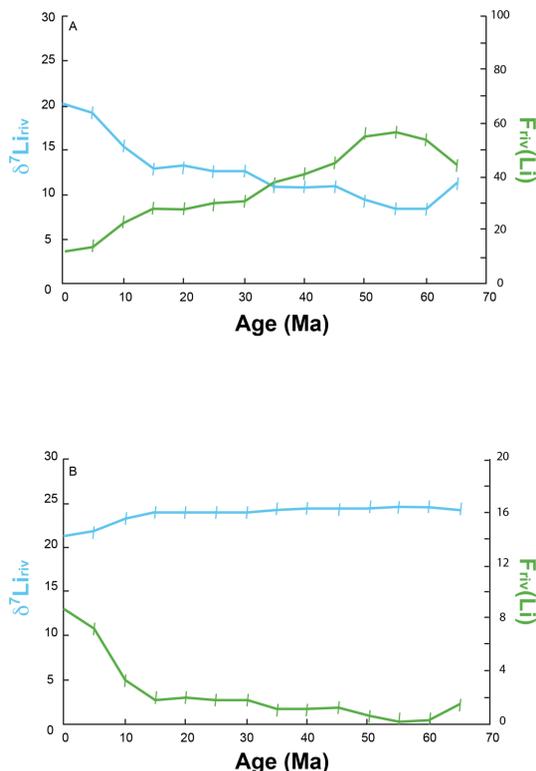


Figure 3. The two solutions of the model described in the text that can both explain the sea-water record (see Eqs. 3–12, and Table 2) F_{riv} is in 10^9 mol yr^{-1} (in green). **(A)** this solution is consistent with calculations performed by Misra and Froelich (2012) since low $\delta^7\text{Li}$ 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.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

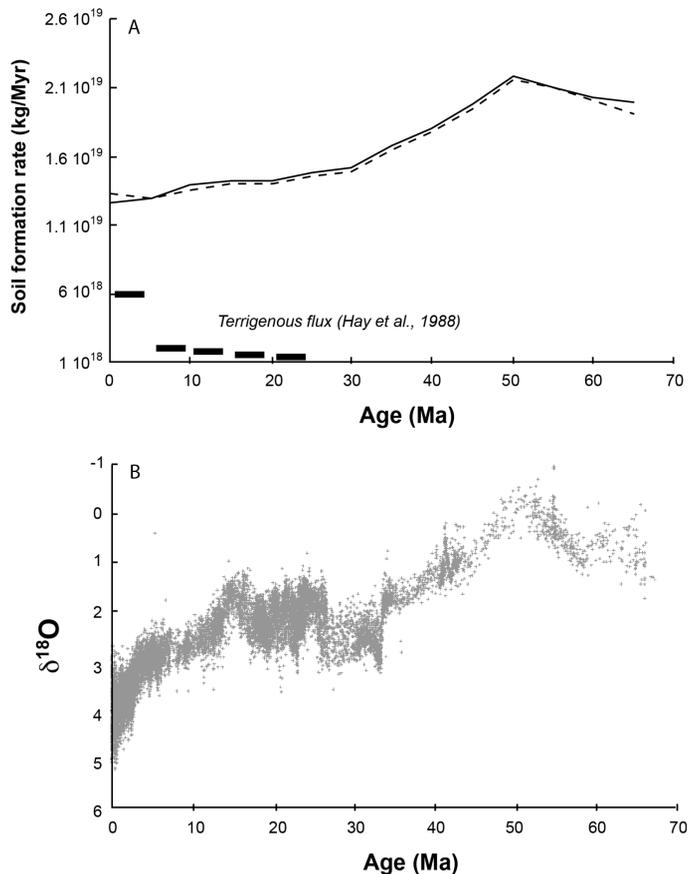


Figure 5. (A) Evolution of soil formation rate as a function of time deduced from the modeling of Li data (see text for more details). A published stimulation of evolution of terrigenous flux is shown for comparison (same unit). (B) Variation of $\delta^{18}\text{O}$ (in ‰) of benthic foraminifera as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

A new approach for modeling the Cenozoic oceanic lithium isotope paleo-variations

N. Vigier and Y. Godderis

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

