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Evolution of Cenozoic seawater lithium isotopes: Coupling of global denudation regime and shifting seawater sinks

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A B S T R A C T

The Li isotopic record of seawater shows a dramatic increase of ∼9‰ over the past ∼60 million years. Here we use a model to explore what may have caused this change. We focus particularly on considering how changes in the "reverse weathering" sinks that remove Li from seawater can contribute to explain the observed increase. Our interpretation is based on dividing the oceanic sink, which preferentially removes light Li, into two components: (i) removal into marine authigenic clays in sediments at low temperatures, with associated high fractionation factors, and (ii) removal into altered oceanic basalt at higher temperatures and resulting lower fractionation factors. We suggest that increases in the flux of degraded continental material delivered to the oceans over the past 60 Ma could have increased removal of Li into sedimentary authigenic clays versus altered basalt. Because altered basalt is associated with a smaller isotopic fractionation, an increasing portion of the lower temperature (authigenic clay-associated) sink could contribute to the rise of the seawater Li isotope value. This effect would moderate the extent to which the isotopic value of continental inputs must have changed in order to explain the seawater record over the Cenozoic. Nonetheless, unless the magnitude of fractionation during removal differs significantly from current understanding, substantial change in the δ^7Li of inputs from continental weathering must have occurred. Our modeling suggests that dissolved riverine fluxes in the early Eocene were characterized by δ^7Li of ∼0 to +13‰, with best estimates of 6.6–12.6‰; these values imply increases over the past 60 Myrs of between 10 and 24‰, and we view a ∼13‰ increase as a likely scenario. These changes would have been accompanied by increases in both the dissolved Li flux from continental weathering and the removal flux from seawater into marine authigenic clays. Increases in δ^7Li of continental input are consistent with a change in the global denudation regime as a result of increasing continental erosion rate through the Cenozoic. Changes in denudation may have meant increasing climate sensitivity of weathering over time but do not require globally supply-limited and thus entirely climate-insensitive weathering in the early Cenozoic.

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1. Introduction

Unraveling the role of global tectonics in the evolution of Earth's carbon cycle and climate during the past 60 Ma has been a hotly debated and contentious problem in the geosciences (France-Lanord and Derry, 1997; Goddéris and François, 1995; Raymo et al., 1988). Mountain uplift has been suggested as a driving force for the climate cooling that has led to the distinctively glaciated climate of the late Cenozoic (Raymo and Ruddiman, 1992; Raymo et al., 1988). Increases in erosion driven by uplift could have stimulated enhanced chemical weathering on the conti-

nents (Gaillardet et al., 1999; Raymo et al., 1988; Riebe et al., 2004; West et al., 2005) and/or changed global sensitivity of weathering to climate (West, 2012), resulting in removal of carbon from the ocean–atmosphere system and sequestration in the sedimentary rock reservoir (e.g., Berner et al., 1983; Urey, 1956). Both the ^{87}Sr/^{86}Sr and ^{187}Os/^{188}Os isotope curves of seawater increase towards more radiogenic values during the Cenozoic, changes that potentially indicate increased continental weathering (Edmond, 1992; Pegram et al., 1992; Peucker-Ehrenbrink and Ravizza, 2000) but are complicated by increased exposure of radiogenic lithologies (Jacobson and Blum, 2000) and changing weathering mineralogy (Li et al., 2007). Although it is possible to infer changes in weathering flux from multi-isotope inversion, e.g. of Os, Sr, and C (Li and Elderfield, 2013; Li et al., 2009), additional information is vital in order to test such model interpretations and to clarify
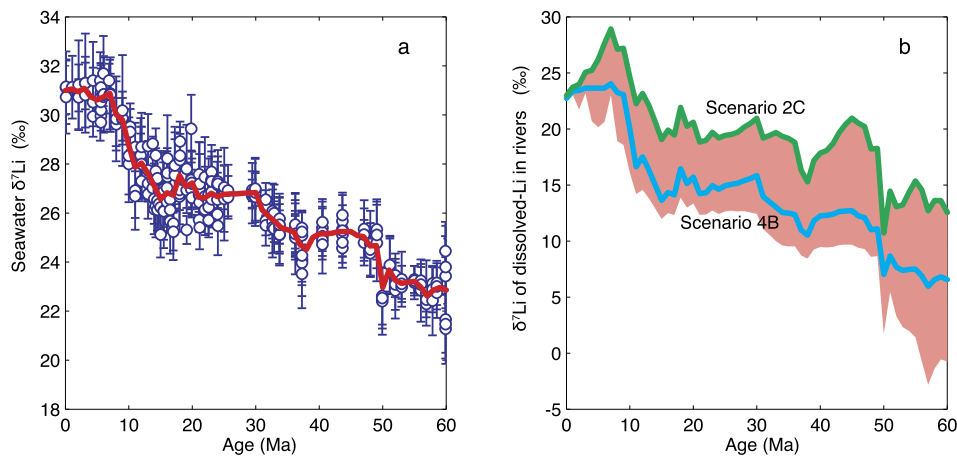
Fig. 1. (a) Lithium isotope ratio of seawater over the past 60 million years based on data from foraminifera, shifted by $+0.6‰$ to match modern seawater δ^7Li value of $31‰$ (Misra and Froelich, 2012). Red line shows smoothed fit to the data determined by a Gaussian filter with a total width of 0.5 Ma. Values of this smoothed fit in a 1 Ma increment are used for δ^7Li$_{sw}$ in our modeling. (b) Variation in the Li isotope composition of the dissolved continental weathering flux delivered to the oceans, based on the full range of δ^7Li$_{diss}$ calculated in our modeling for a range of parameter combinations and flux reconstructions in the Cenozoic Li cycle. All model results require some change in δ^7Li$_{diss}$ since 60 Ma, but this may have been as small as $\sim 10‰$. Cyan and green lines show solutions for scenarios 4B and 2C respectively (cf. Table 2, Fig. 2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

whether early Cenozoic erosion could have been so low as to inhibit climatic regulation of weathering, and thus the feedback that stabilizes long-term climate (cf. Edmond and Huh, 2003; Froelich and Misra, 2014).

The stable isotope composition of lithium (δ^7Li) in seawater holds valuable information, since the dissolved δ^7Li from weathering is thought to be related to continental silicate weathering (Huh et al., 1998, 2001; Misra and Froelich, 2012), but is not thought to be strongly lithology dependent, unlike Sr and Os (Huh et al., 1998, 2001; Kısakűrek et al., 2005; Millot et al., 2010b). Continental fluxes of dissolved Li are associated specifically with silicate mineral dissolution, which governs continental CO_2 consumption over geologic time (Berner et al., 1983; Urey, 1956; Walker et al., 1981). Li fluxes are minimally influenced by carbonate weathering or biological processing, which complicate many other isotopic systems. In data from global rivers, the correlation between dissolved δ^7Li and the ratio of [Si]/(total dissolved ion concentration), corrected for evaporite contributions, suggests a relationship between dissolved lithium isotope ratio and silicate "weathering intensity" (Huh et al., 2001). In general terms, weathering intensity reflects the fraction of the total material available for dissolution that has been chemically weathered (Fontorbe et al., 2013; West, 2011). If rates of physical erosion increase, but silicate chemical weathering remains constant, weathering intensity should drop and, to first order, this should be reflected in an increase in the dissolved δ^7Li from weathering at the global scale (e.g., Bouchez et al., 2013).

The δ^7Li isotopic composition of fossil planktonic foraminiferal calcite (Hathorne and James, 2006; Misra and Froelich, 2012) shows a significant ($\sim 9‰$) increase over the Cenozoic (Fig. 1a), much like the changes in Sr and Os. The foraminiferal data have generally been taken as a faithful record of seawater δ^7Li, implying a shift toward significantly heavier seawater Li isotope composition with time. This can be explained by a change in the δ^7Li of the dissolved weathering flux because of a transition from a high intensity weathering regime characterized by largely congruent, supply-limited weathering in the early Cenozoic, to a low intensity weathering regime with more Li trapped in secondary continental clay minerals in the rapidly-eroding present-day (Misra and Froelich, 2012). Such a transition would have important implications for how erosion, weathering, and the carbon cycle have evolved over the past 60 Ma (e.g., Froelich and Misra, 2014), and would general-

ly support the hypothesis that large-scale tectonic changes may have driven global cooling.

However, it remains unclear whether other processes might explain the foraminifera δ^7Li record. In their interpretation, Misra and Froelich (2012) focused on one "end-member" case where all of the change in seawater δ^7Li over the Cenozoic is attributed to changes in continental weathering. Several additional fluxes and processes, such as changes in the magnitude of global weathering fluxes of dissolved Li to the oceans, or changes in the fluxes or isotope fractionation associated with removal of Li from seawater, can affect seawater isotopic composition. Here we assess these effects on the Li cycle and present a model for plausible Cenozoic scenarios that can explain the seawater record. We focus our attention on changes in the isotopic fractionation associated with removal of Li from seawater, and how they may relate to changes in continental fluxes to the oceans. We use our model to address the question of whether the Cenozoic δ^7Li seawater record requires change in the isotopic composition of continental inputs, and how much change is required.

2. Conceptual framework

2.1. The oceanic Li isotope budget and the role of weathering intensity

The main sources of Li to the ocean are river water and high temperature hydrothermal fluids, which have modern fluxes of similar magnitude, of about 10×10^9 and 13.0×10^9 mol/yr respectively (Table 1). The average δ^7Li value of modern river water is about $23‰$ (Huh et al., 1998; Misra and Froelich, 2012), much higher than the value of $8.3‰$ for hydrothermal fluids (Misra and Froelich, 2012). To achieve a steady state ocean in the present, the δ^7Li value of the total oceanic Li sink should balance the value of the total inputs (Fig. 2a), requiring an average sink with δ^7Li $\sim 15‰$ over timescales on the order of the residence time of Li in the oceans (~ 1 Ma). Comparing this value to that of modern seawater ($31‰$) implies a $\sim 16‰$ net isotopic fractionation during the removal of Li from seawater in the present day, with preferential uptake of light Li during removal (Misra and Froelich, 2012).

If this $16‰$ isotopic fractionation remained constant in the past, the δ^7Li value of seawater at 60 Ma, about $22‰$, would require an average δ^7Li of $6‰$ for both the total inputs and total outputs to the oceans at this time. This value is lower than that of the hydrothermal input ($8.3‰$), posing a balance problem unless rivers