A lithium isotope perspective on the carbon and silicon cycles evolution

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The evolution of the global carbon and silicon cycles are thought to have contributed to the long-term stability of the Earth's climate[1–3]. Many questions remain, however,

regarding the feedback mechanisms at play and more quantitative constraints on the sources and sinks of these elements in the Earth's surface environments are lacking[4–12]. Here we argue that the lithium isotope system can be used to track processes controlling the long-term carbon and silicon cycles. Based on the analysis of over 600 shallow-water marine carbonate samples from 101 stratigraphic units, we construct a new carbonate lithium isotope record spanning the past 3 billion years. The data suggest an increase in the carbonate lithium isotope values over time, which we propose was driven by long-term changes in the lithium isotopic conditions of seawater rather than changes in the alterations of older samples. Based on a mass balance modelling approach, we propose that the observed trend in lithium isotope values reflects a transition from the Precambrian carbon and silicon cycles to those more similar to the present day. We speculate that this transition may be linked to a shift to a biologically controlled marine silicon cycle and the radiation of land plants[13,14].

Earth has maintained a clement climate for the vast majority of the past 3.5 billon years, despite large changes in solar luminosity, atmospheric oxygen concentrations, and crustal evolution[1]. Climate stability has allowed for Earth's persistent habitation and proliferation of complex life over billion-year time scales. Feedbacks within the coupled carbon (C) and silicon (Si) cycles maintain this stability by regulating atmospheric carbon dioxide levels[2], as exemplified by the continental silicate weathering feedback which removes atmospheric carbon dioxide during continental weathering and transfers silicon to the ocean. This climate dependent mechanism is the most commonly invoked process stabilizing Earth's long-term climate[2,3].

The idea that the terrestrial silicate weathering feedback played the dominant role in climate regulation through Earth's history has been challenged in the last decade[4,5]. For example, there have been several recent suggestions that sedimentary and hydrothermal processes in the marine realm strongly affected atmospheric carbon dioxide levels earlier in Earth's history[6–9]. It has been proposed that extensive authigenic clay formation in marine sediments (reverse weathering) in Si-rich oceans was a key factor leading to a warm climate through most of Earth's history[8,10]. In this view, the evolutionary radiation of siliceous organisms (sponges, radiolarians, and later diatoms) forced a drop in dissolved marine Si levels and hence a marked decrease in the extent of reverse weathering. There has also been extensive debate about whether, how, and when land plants transformed the silicate weathering feedback[11,12].

Disagreement on fundamental aspects of the long-term C cycle demands new empirical records that provide constraints on the evolution of the C and Si cycles over geological time.

The Li isotope system can be used to track processes controlling the long-term C and Si cycles. Seawater Li isotope values are strongly influenced by the global extent and dominant modes of clay formation and therefore can be used to determine global weathering regimes[15]. Lithium in the crust is predominantly found in silicate minerals and the largest Li isotope fractionations occur during the low–temperature formation of secondary silicate minerals—largely clays. Clay minerals preferentially incorporate the lighter Li isotope (^{6}Li), leaving residual waters enriched in the heavier isotope (^{7}Li)[16]. Clay formation occurs on land during incongruent silicate weathering and in the oceans during off-axis seafloor alteration and during reverse weathering in sediments. Therefore, clay formation in the marine and terrestrial realms has the potential to drive the dissolved seawater Li isotope signature towards values heavier than the average crust (crustal value is ~0‰; Ref. 17)[15,16,18,19]. Tracking clay formation and its link to continental and marine weathering processes, the Li isotope system is a powerful tool for investigating the long-term controls of the C and Si cycles.

Given that carbonates can be a reliable archive of seawater δ^{7}Li [18,20,21], we generated a new carbonate Li isotope record through Earth's history. We analysed over 600 shallow-water marine carbonate samples from 101 stratigraphic units that range in age from 3.0 Ga to the modern (Fig. 1 and SI Tables 1 and 2). Our sampling focused on micritic carbonates but also included grainstones, reef cements, microbialites, and brachiopods. Samples were selected using a combination of standard and cathodoluminescence petrography (see SI for additional information on sampling protocols and selected units).

A major concern with all carbonate-based proxies is whether the samples record primary signals or if they have been overprinted[22]. The Li isotopic composition of shallow-water marine carbonates in the sedimentary record depends on both the primary mineralogy of the sediment (aragonite vs. calcite) and the type of alteration during early burial[23]. Additionally, carbonate samples can undergo late-stage alteration. Given potential uncertainties associated with these processes, we tested the extent to which we can reconstruct seawater values from our carbonate record in four ways (see SI). First, we generated a complementary record to our samples from well-preserved early marine cements—the carbonate component that can be most robustly screened for diagenetic alteration in both Phanerozoic and Precambrian rocks[24] (see SI Table 1;

Supplementary information). Second, to gauge the effects of mineralogy and diagenesis, besides petrology, we analysed all samples for major/minor/trace element ratios. Third, following Ref. 25, we focused our sampling on carbonate units that are not from carbon isotope excursions—given that these excursions are interpreted as being a signal for either short-term carbon cycle perturbations or diagenetic events (see SI)[26,27]. Lastly, a subset of our sample suite was analysed for Ca isotopes, which has emerged as a powerful tracer of the extent and type of diagenetic alteration in shallow-water marine carbonates[28,29].

Our dataset suggests a dramatic change in carbonate Li isotope values through time (Fig. 1 and SI Table 2). Cainozoic and Mesozoic values range from 14.6‰ to 29.5‰ with an average of 23.1±3.8‰ 1STD (n = 45). This is similar to foraminifera records from the Cainozoic that range from 20.1‰ to 33.7‰ with an average of 25.9±2.7‰ 1STD (n = 319)[18,30,31]. Low carbonate δ^7Li values persist through most of the Palaeozoic with a mean δ^7Li = 10.1±4.3‰ 1STD (n = 263) (Fig. 1). Precambrian values range from -3.8‰ to 23.5‰ but with a mean δ^7Li = 7.7±5.7‰ 1STD (n = 217). Basic descriptive statistics suggests there are significant shifts in carbonate Li isotope values through time. For instance, a Welch's ANOVA test demonstrates that δ^7Li values are significantly different ($F = 273.6$, $p < 0.001$) for samples from present to end-Mesozoic (0 – 252 Ma, n = 45), from samples spanning the Palaeozoic (252 – 541 Ma, n = 263), and samples spanning the Precambrian (541 – 3,000 Ma, n = 217). Critically, these low values are also found in well-preserved micro-drilled marine cements (Figs. 1, 2). The general trend in the δ^7Li record in carbonates resembles, to a first-order approximation, the trend in the carbonate strontium isotope record through time (Fig. 1c).

Our observed trend in Li isotope values could be a signal of varying extents of alteration or a signal for environmental evolution. However, several lines of evidence are inconsistent with the premise that our carbonate Li isotope record reflects varying extents of alteration. Importantly, the observation that low carbonate δ^7Li values, relative to modern, persist for the majority of Earth's history, even after the data set is screened for detrital contamination and diagenetic tracers, suggests an explanatory mechanism other than only alteration in our samples. Shallow-water carbonate Li isotope values are likely to be 0‰–10‰ lighter than coeval seawater values, depending on the original mineralogy and the mode of burial diagenesis (see SI; Ref. 23). Yet, critically, Sr/Ca ratios and $\delta^{44/40}$Ca analysis can be used to track the burial offset from seawater in shallow-water carbonates[23,32] (see SI), and there is no evidence for a systematic change in the mode of early marine diagenesis through time that could explain the observed ~ 15‰ increase

in mean carbonate δ^7Li values (or *a priori* reason to expect such a change). Additionally, we used a suite of commonly employed geochemical filters to constrain primary mineralogy (Sr/Ca, Mg/Ca), track detrital contamination (Al/Ca, Rb/Ca) and diagenetic alteration (Mn/Sr, Pb/Ca) (see SI for further detail). Samples screened using these methods show similar trends in the unscreened Li isotope data (Fig. 1; See SI). Nonetheless, we acknowledge that some units in our study may have experienced late-stage alteration that is not easily screened with typical elemental tracers. Critically, however, late-stage diagenetic alteration appears to result in a shift towards higher δ^7Li values[33], indicating that our carbonate record of lighter values in older samples is unlikely to reflect a diagenetic bias. Building upon previous work on the effects of alteration on the Li isotope system[33], we argue that if detrital contribution can be ruled out, the lower boundary of the δ^7Li values will most accurately represent seawater evolution. With this framework, the Li isotope record would be interpreted in a similar fashion to the scatter in the long-term Sr isotope records (e.g., Ref. 34; Fig. 1d). Further, carbonate cements with exceptionally well-preserved fabrics—samples that could not have undergone extensive alteration after deposition (see Refs. 24,35; Fig. 1)—display the same trend as our larger bulk rock dataset.

Using our carbonate record, (filtered for detrital contamination, and assuming an offset of 4±5‰ from seawater; see SI; following Ref. 23), we were able to reproduce previously estimated Cainozoic (Fig. S14), as well as Mesozoic and Palaeozoic δ^7Li_{SW} values (Fig. 1a). Assuming this same offset for Precambrian samples, we estimate Precambrian δ^7Li_{SW} values were on average 6-16‰, notably lighter than the modern oceans (31‰; Ref. 36). As with other isotope systems[37], it will be critical to verify our reconstructed Li isotope trends in another sedimentary archive. Nonetheless, we propose that the most straightforward explanation of our carbonate Li isotope dataset is that there were significant changes in seawater Li isotope values across Earth's history.

To evaluate the mechanisms that could be driving long-term changes in seawater Li isotope values, we employed a stochastic mass balance modelling approach (Fig. 3). Specifically, we use an isotope mass balance model to conduct solution space testing. This provides a means of exploring possible configurations of the Li isotope system responsible for the long-term shift that we observe in estimated δ^7Li_{SW} values. In our simulations, we solve Li isotope mass balance at 1 Myr time intervals and allow for a wide range of possible values for high- and low-temperature hydrothermal fluxes, riverine fluxes, and their isotopic values (Table SI 3). At each

time-step, we employ a Monte Carlo routine to re-sample the uniformly distributed key parameters 1,000 times, with acceptable solutions being the ones that match our estimated, error-bounded, Li isotope record (Fig. 3; see SI for the model derivation).

With our modelling approach, persistently low δ^7Li_{SW} values in the Precambrian (Fig. 3 and Figs. S18-23) appear to require changes in terrestrial and marine Li cycling in Earth's past relative to the modern. For instance, the only Earth system (i.e., the prominent combination of Li cycle parameters) that fits our data from the Precambrian (Fig. 3) requires rivers with low Li isotope values (δ^7Li_{Riv} < 10‰) together with muted isotope fractionation (Δ^7Li < 10‰) during Li burial in the marine realm through marine authigenic clay formation (maac) and low-temperature basalt alteration (lowT). Low Precambrian δ^7Li_{SW} could be related to elevated high-temperature hydrothermal Li fluxes, which are a source of relatively light Li (~6.3‰; Ref. 38). However, most geophysical models show that near modern hydrothermal activity was reached by the Paleoproterozoic[39], and some estimates suggest constant hydrothermal heat flux[40], which would lead to approximately constant, long-term hydrothermal Li fluxes. Therefore, consistent with our modelling results, enhanced high-temperature hydrothermal fluxes are likely not responsible for the low δ^7Li_{SW} values through most of Earth's history.

The proliferation and diversification of land plants over much of the Phanerozoic has been hypothesized to have fostered more extensive formation and retention of clay minerals in the terrestrial realm[13]. Our work—which calls for an increase through time in δ^7Li_{Riv} values (Fig. 3)—supports this idea. There are multiple ways in which plants may have changed weathering, but fostering soil development and increasing water-rock interaction times is one way to increase the probability of clay formation[13]. There is some mineralogical evidence that also supports the hypothesis that prior to the rise of land plants there was more limited paedogenic clay mineral formation[41]. Weathering regimes may have continued to shift until the rise to dominance of angiosperms at roughly 80 Ma[14].

Extensive clay formation in the marine sediment column, as has been proposed for the Precambrian[8,10], is one obvious way of changing the marine Li cycle. Our prediction of a more limited effective isotope fractionation during Li burial (Δ^7Li_{maac} and Δ^7Li_{lowT}) earlier in Earth's history can be linked to rapid rates of clay formation, which could have led to high rates of Li uptake and the reaction sites being in restricted contact with the reactant pool (seawater)[42]. For the majority of Earth history, without the presence of Si-biomineralizers, seawater was highly

oversaturated with respect to Si phases, which could have resulted in rapid and extensive clay formation[8]. This style of reverse weathering and Li removal is likely to have limited the effective Li isotopic fractionation (see SI; Ref. 42). The progressive decrease in marine Si concentrations over the Phanerozoic[43] linked to the transition to a more biologically controlled Si cycle may, therefore, may have driven a shift in seawater Li isotope values.

The apparent common occurrence of low δ^7Li_{SW} values in the Precambrian and the early Palaeozoic, supports the premise that the carbon cycle operated in a fundamentally different mode for the majority of Earth's history compared to the present day. While we cannot use Li isotope values to constrain a single Earth system, our modelling work suggests there was a major shift in clay factories through Earth's history—with a likely increase in clay formation on land and a decrease in clay formation in the oceans. Clay formation is a critical part of the coupled C-Si cycles, suggesting that the mode of climate regulation on Earth has changed dramatically through time. The shift from a Precambrian Earth state to the modern state can likely be attributed to significant biological innovations—the radiation of sponges, radiolarians, diatoms, and land plants. Further, our record suggests that the development of a more modern-style carbon cycle tied to these ecological transitions was protracted instead of being marked by step changes.

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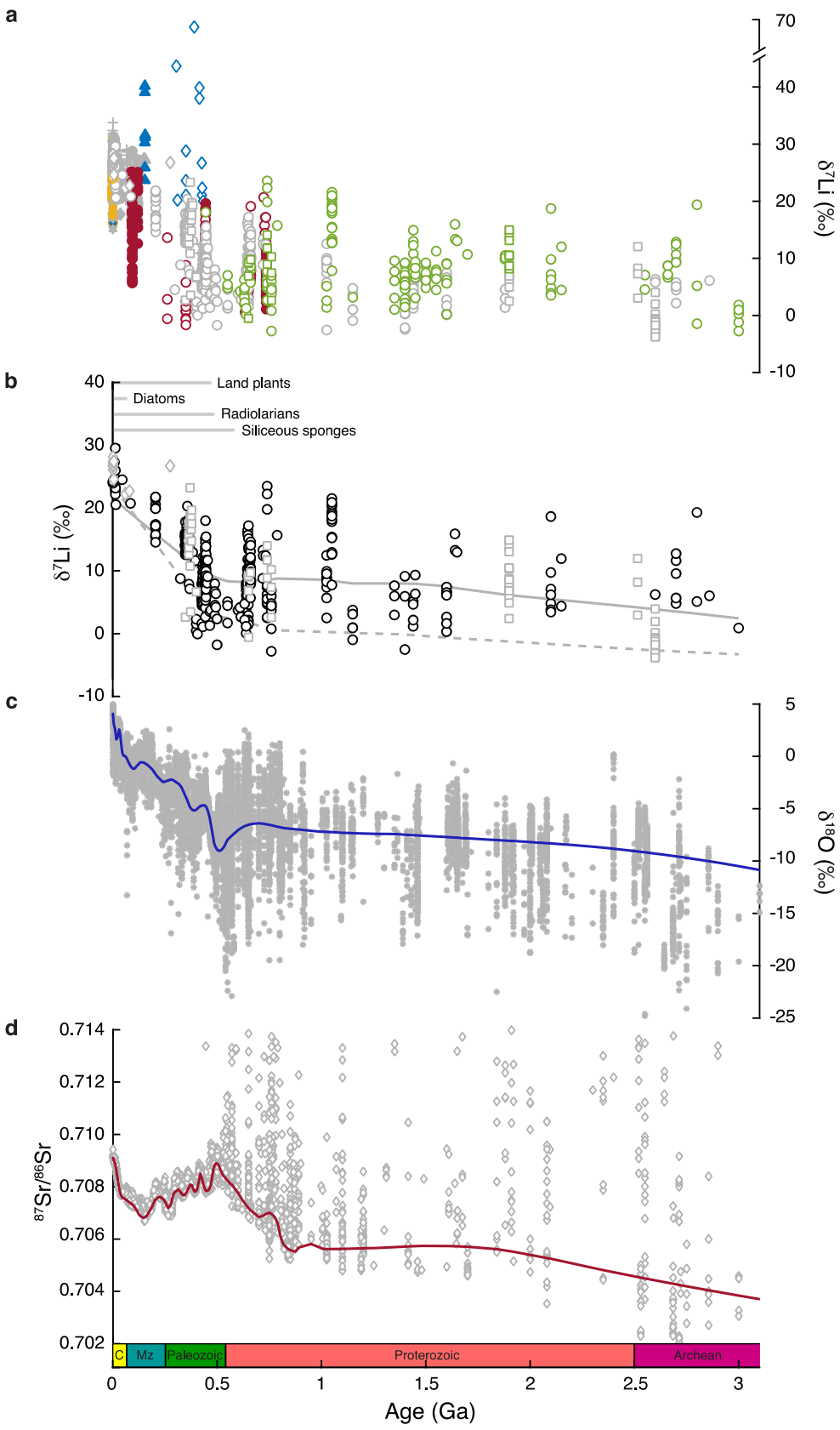

a
70
40
30
20
10
0
-10
δ7Li (‰)
b
Land plants
Diatoms
Radiolarians
Siliceous sponges
40
30
20
10
0
-10
δ7Li (‰)
c
5
0
-5
-10
-15
-20
-25
δ18O (‰)
d
0.714
0.712
0.710
0.708
0.706
0.704
0.702
87Sr/86Sr
C
Mz
Paleozoic
Proterozoic
Archean
0
0.5
1
1.5
2
2.5
3
Age (Ga)

Figure 1: Isotope records in carbonates through time. a A compilation of lithium isotope values measured in different types of carbonates, including the new data from this study (open symbols) and previously published data (closed symbols) (n_{total} = 1396; Refs. 18,20,21,23,30,31,33,44-46). Grey – calcite, yellow – aragonite, green – dolomite, blue - diagenetically altered carbonates, and red – samples from periods of known carbon isotope excursions. Shapes denote different types of carbonate archives: squares – cements, crosses – foraminifera, diamonds – brachiopods, triangles – belemnites, hexagons – corals. **b** New filtered lithium isotope data ($n_{filtered}$ = 525; n_{new} = 712). Samples with indications of diagenetic alteration or of high detrital input (i.e., with Al/Ca > 0.00054 ppm/ppm) are omitted. Light grey squares denote new data from well-preserved marine cements (n = 74). Light grey diamonds denote brachiopods. Light grey solid curve denotes a LOWESS fit of the mean of the data. Light grey dashed curve denotes a LOWESS fit of the lowest ten percent of the values. **c** Oxygen isotope values measured in carbonates (Ref. 47). Blue curve denotes a robust loess fit of the data. **d** Strontium isotope ratios measured in carbonates (Refs. 32,48). Red curve denotes a robust loess fit of the lowest ten percent of the values.

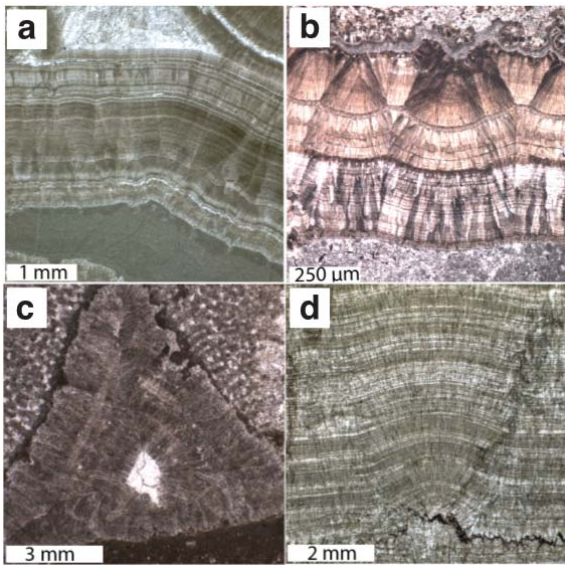


Figure 2: Thin section photomicrographs of representative well-preserved carbonates from this study. a,b Neoproterozoic carbonates: **a** Multiple generations of dolomite (and mimetically dolomitised calcite) marine cements and micrite from the Tonian Devede Fm., Namibia; **b** Well-preserved dolomitised calcite cements from the Tonian Beck Spring Dolomite, USA. **c** Paleozoic carbonate: calcite marine-cemented sponge from the Devonian Napier Formation, Australia. **d** Precambrian carbonate: calcite seafloor fans of the Neoarchean Campbellrand Gp., South Africa. The presence of well-preserved carbonate textures rules out extensive secondary alteration.

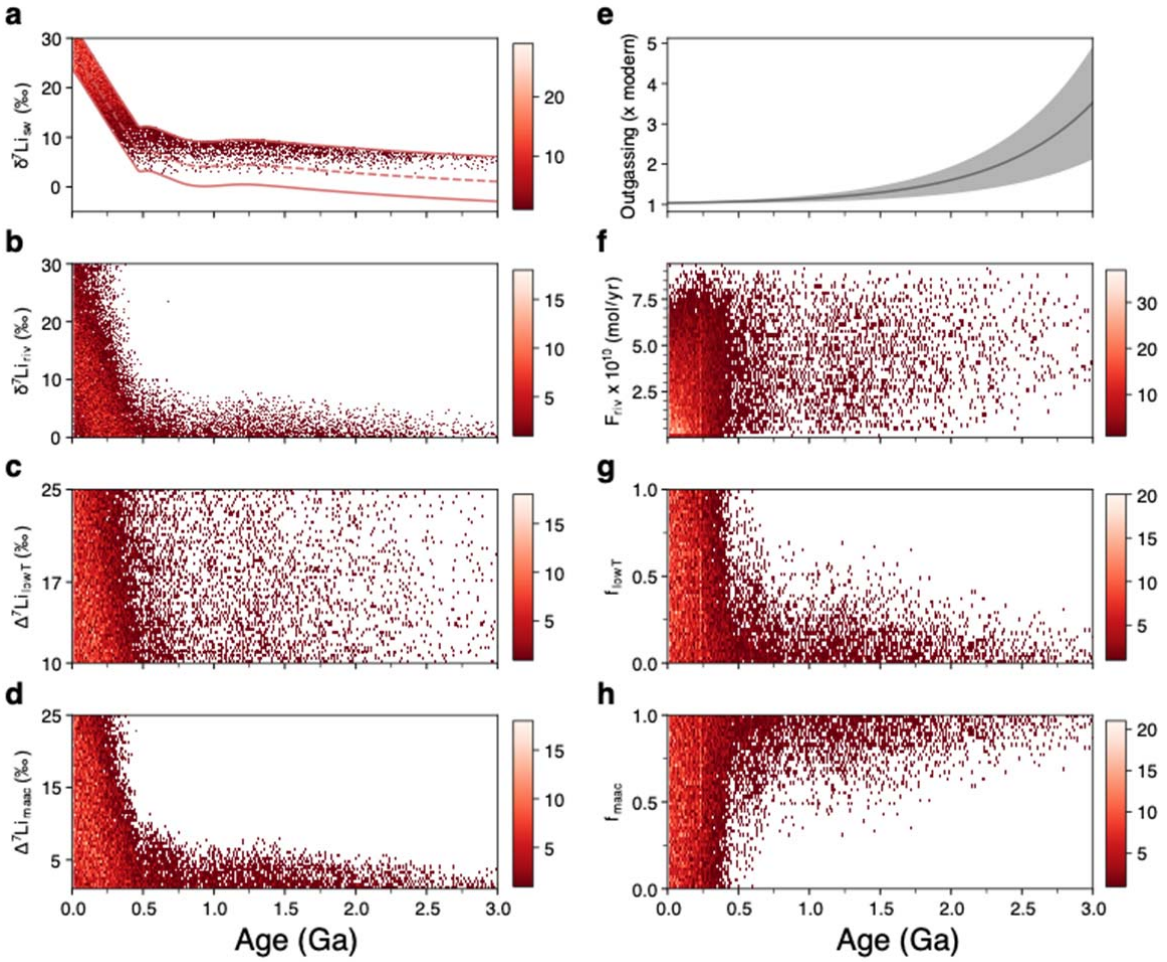


Figure 3. Two-dimensional density heatmap of lithium isotope mass balance results. Each panel indicates the density of the parameters that successfully match our empirically determined, LOWESS-smoothed Li isotope record (LOWESS conducted on lower ten percent of data (dashed line in (a)), with upper and lower solid filtering bounds) through Earth's history. The light red represents higher counts per bin, red represents lower counts per bin, and white regions represent solution space that cannot satisfy a steady-state ($F_{in} = F_{out}$) Li seawater isotope value as determined by our empirical record. Panels show **a** the Li isotope value of seawater, **b** riverine Li isotope value, **c** the isotopic fractionation associated with Li removal from seawater during basalt alteration (Δ^7Li_{lowT}), **d** the isotopic fractionation associated with Li removal from seawater during marine authigenic clay formation (Δ^7Li_{maac}), **e** outgassing estimates from Refs. 39,49,50, **f** the riverine Li flux, **g** the proportion of Li removed through basalt alteration (f_{lowT}), and **h** the proportion of Li removed through marine authigenic clay formation (f_{maac}). F_{HT} is scaled linearly to a mean value of outgassing estimates. The LOWESS curve is regressed through our original data with an applied calcite fractionation from seawater (Δ^7Li = -4‰). The

lower filtering bound is -4‰ from the LOWESS curve, representing fluid buffered solutions, whereas the upper bound is +5‰ from the LOWESS curve, representing the potential for any samples to be aragonite.

a

b

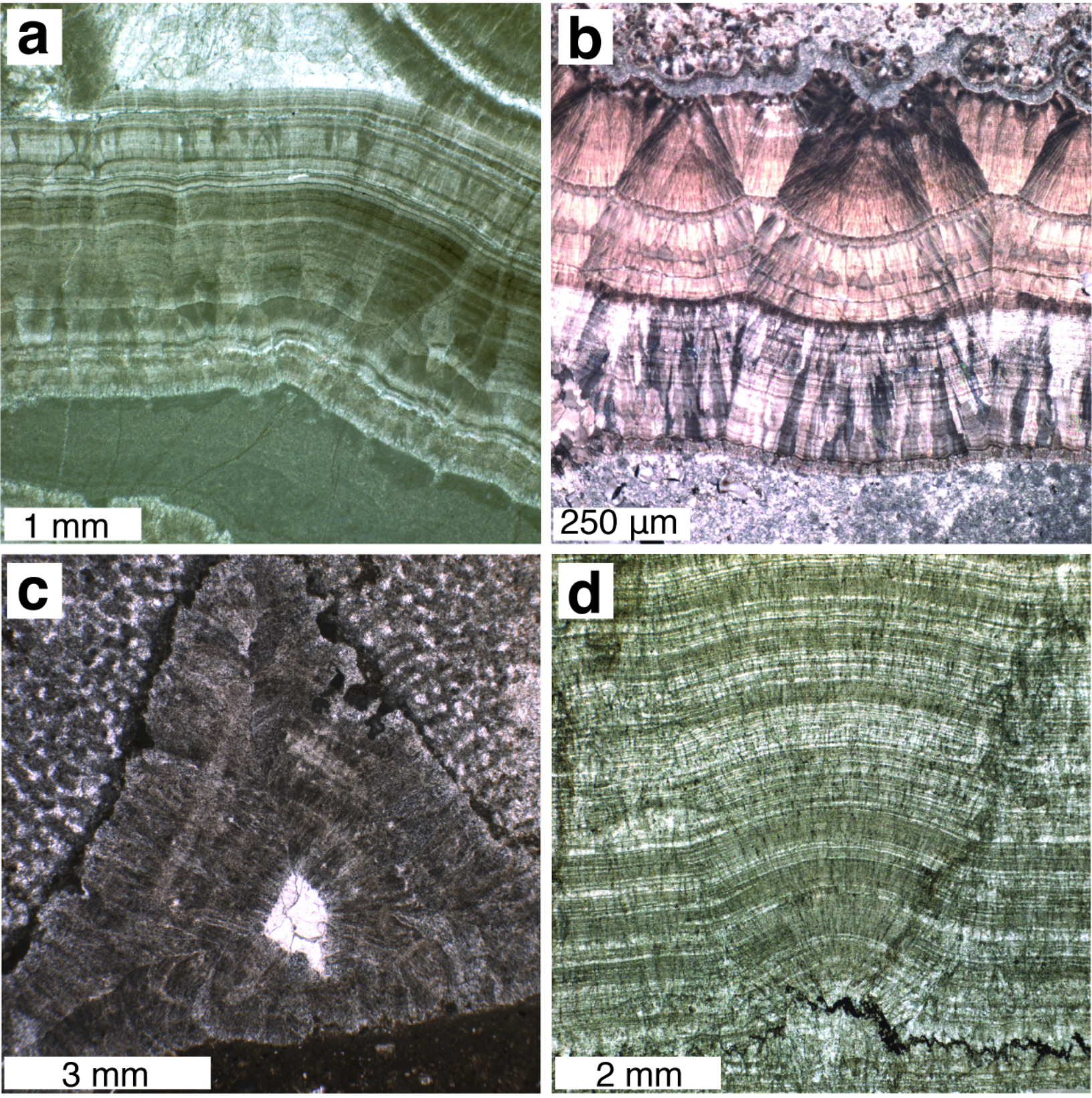
c

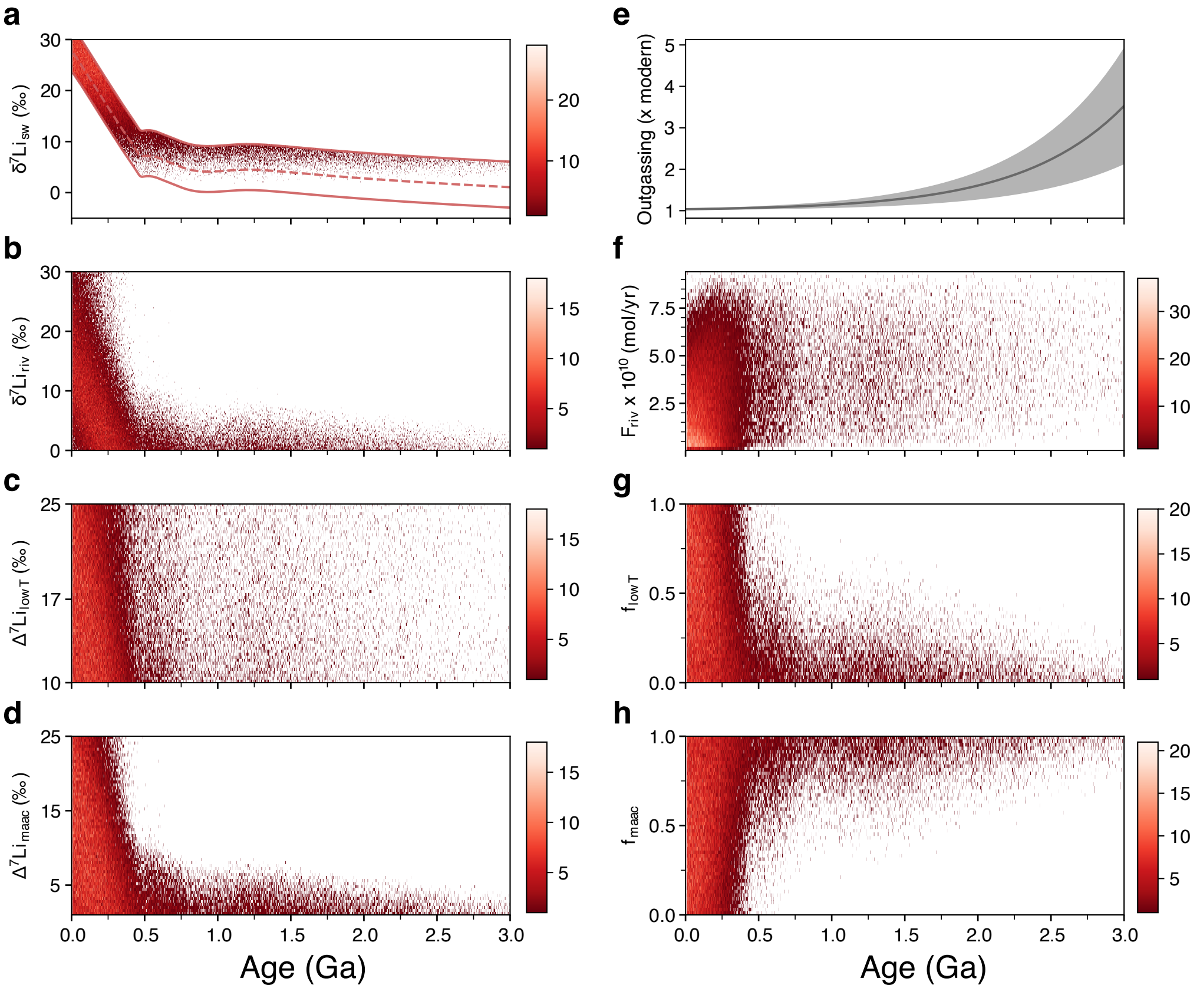
d

Land plants
Diatoms
Radiolarians
Siliceous sponges

C
Mz
Paleozoic
Proterozoic
Archean

Age (Ga)


a
1 mm
b
250 µm
c
3 mm
d
2 mm


a
b
c
d
e
f
g
h
δ^7Li_{sw} (‰)
δ^7Li_{riv} (‰)
Δ^7Li_{lowT} (‰)
Δ^7Li_{maac} (‰)
Outgassing (x modern)
F_{riv} x 10^{10} (mol/yr)
f_{lowT}
f_{maac}
Age (Ga)
Age (Ga)