Paleogeographic forcing of the strontium isotopic cycle in the Neoproterozoic

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ABSTRACT

The period spanning from 825 to 540 Ma is characterized by major changes in the surficial Earth system. This extraordinary interval starts with the breakup of the Rodinia supercontinent and eruption of a series of large igneous provinces and ends with the assembly of Gondwana, giving rise to the Pan-African orogenies. This paleogeographic reorganization is accompanied by a global climatic cooling, including the paroxysmal Cryogenian “snowball” glacial events. The 87Sr/86Sr of seawater displays a major long-term rise over this interval that is punctuated by episodic, smaller declines and inflections. We use a coupled deep time climate-carbon numerical model to explore the complex role of tectonics and climate on this distinct evolution in seawater 87Sr/86Sr. We show that the modulation of the weathering of the erupted large igneous provinces by continental drift explains the changes in seawater 87Sr/86Sr from 800 to 635 Ma. The subsequent sharp rise in seawater 87Sr/86Sr from 635 to 580 Ma is the result of erosion of radiogenic crust exposed in the Pan-African orogens. Coeval evolution of atmospheric CO2 displays a decrease from about 80 times the pre-industrial level around 800 Ma to 5 times just before the beginning of the Phanerozoic.

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1. Introduction

The strontium isotopic composition of seawater over the last 850 million years, as recorded in carbonate minerals, reveals three major long-term trends (Fig. 1). First, between ca. 850 and 500 Ma, 87Sr/86Sr rises in two broad steps from 0.706 to 0.709 (Halverson et al., 2007). This Neoproterozoic increase in 87Sr/86Sr is followed by a long-term (> 300 m.y.), net decrease from the late Cambrian to the Jurassic (Veizer et al., 1999; McArthur et al., 2012). Finally, 87Sr/86Sr increases from 0.707 in the Jurassic to 0.709 at present day, with an inflection to a much steeper slope beginning ca. 40 Myr ago (De Paolo and Ingram, 1985).

The causes of trends in seawater Sr isotope ratios have been intensely debated over the last 30 years, with most models emphasizing the relative contributions of hydrothermal versus continental Sr fluxes to seawater. Many papers have focused on the rise over the last 40 Ma, for which the record is most complete (De Paolo and Ingram, 1985). The dominant interpretation for this abrupt increase is that it records the influence of the Himalayan orogeny in exposing large volumes of highly radiogenic (i.e. high 87Sr/86Sr) rocks to continental weathering (Edmond, 1992; Galy et al., 2002; Myrow et al., 2015). However, alternative models have been proposed. Zachos et al. (1999) proposed that the increased flux of radiogenic Sr to seawater instead reflects the onset of Antarctic glaciation and its role in physical breakdown of radiogenic rocks, thus facilitating chemical weathering. Focusing instead on the hydrothermal Sr source to seawater, Coogan and Dosso (2015) argued that the Cenozoic rise in 87Sr/86Sr can be explained by a decrease in the off-axis Sr flux due to lower bottom-water temperatures attending global cooling at this time.

Less attention has been paid to the longer-term changes in seawater 87Sr/86Sr. By analogy to the late Cenozoic, the Neoproterozoic rise, or at least the steep increase in the Ediacaran Period, has been related to the impact of the Pan-African orogenies on the strontium isotopic cycle (Derry et al., 1989). But the mechanism behind the earlier Neoproterozoic, longer-term changes (> 100 Myr) remains obscure, in particular because it contradicts traditional models that would imply that continental break-up (i.e. of Rodinia) should increase the hydrothermal Sr.
Recent studies have offered new perspectives on the strontium cycle. The role of island arc weathering has been identified as an important driver of the oceanic strontium isotope budget, potentially accounting for 60% of the low radiogenic Sr input into seawater (Allègre et al., 2010). Van Der Meer et al. (2014) proposed that the length of subduction zones, if used for scaling the input of mantle strontium into the ocean, can explain the main features of the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ over the last 250 million years. Young et al. (2009) and Nardin et al. (2011) argued that the general decline in the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the early Paleozoic, and specifically during the Ordovician, might be related to the enhanced weathering of young volcanic rocks with time. In this scenario, the engine driving secular evolution in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is a response to the enhanced weathering of young, unradiogenic basalt and andesite. In contrast, as break-up proceeds, the margins of old continental shields are uplifted and their interiors increasingly exposed to precipitation, potentially elevating the flux of radiogenic strontium to the oceans. Based on this qualitative reasoning, Halverson et al. (2007) suggested that the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ should increase during the break-up of a supercontinent as the relative importance of continental weathering increases at the expense of arc weathering.

Such a scenario has not been tested quantitatively. Nor did this conceptual model account for the role of emplacement of large igneous provinces (LIPs), which are associated with supercontinental break-up (Courtillot et al., 1999), or subsequent Himalayan-style orogenesis, which follows continental break-up. In this contribution, we explore the relative role of paleogeography and these other processes related to the supercontinental cycle on the long-term evolution (10^7 years) of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the Neoproterozoic using the Earth System Model for the deep time GEOCLIM.

2. Methods

We tested the impact of Rodinia break-up, of the weathering of young volcanic arcs and LIPs, and of the Pan African orogen on the Neoproterozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through the application of the spatially resolved numerical model, GEOCLIM, which we summarize here. A complete description of GEOCLIM can be found in Donnadieu et al. (2006) and in Goddéris et al. (2014).

2.1. The GEOCLIM model

GEOCLIM couples a 10-box model describing the biogeochemical cycles of carbon, oxygen, alkalinity, phosphorus, strontium, and its isotopic budget to a spatially resolved climate model. The continental weathering fluxes are calculated with a spatial resolution of 7.5° longitude by 4.5° latitude. The boundary conditions are the amount of energy received from the sun by the Earth, the continental configuration, the solid Earth degassing, the continental topography, and the spatial distribution of different continental lithologies. Continental weathering is calculated for each continental grid cell as a function of mean annual local temperature and runoff (Dessert et al., 2003; Oliva et al., 2003). Here, GEOCLIM is run in a steady-state mode. This means that we calculate the level of atmospheric CO2 and associated spatially resolved climate at which CO2 consumption by continental silicate weathering balances the prescribed solid Earth CO2 degassing flux (Walker et al., 1981). In other words, we calculate the steady-state CO2 and climate for each set of boundary conditions. We then calculate seawater $^{87}\text{Sr}/^{86}\text{Sr}$ assuming that the strontium cycle is in steady-state, a reasonable assumption for the temporal resolution of our simulations (one simulation every 30 to 50 million years).

The spatial resolution of the climate model is 7.5° long × 4.5° lat. Continental weathering fluxes are calculated at the same resolution. The model accounts for four lithologies: shield rocks (i.e. old continental crust), fresh basalts surfaces (LIPs), volcanic arcs, and carbonate rocks. LIPs and volcanic arcs are located on each map according to geological constraints (see boundary conditions). The remaining spaces on the continental surfaces are filled by shield and carbonate rocks. The weathering flux for LIPs is calculated as follows (assuming a basaltic lithology) (Dessert et al., 2003):

$$f_{\text{LIP}} = \sum_{j=1}^{n_{\text{grid}}} \phi_{\text{LIP}} \times \text{area}_j 	imes f_{\text{LIP}}$$

where $n_{\text{grid}}$ is the number of continental grid elements, area$_j$ the area of the grid element $j$, and $\phi_{\text{LIP}}$ is the fraction of the grid element covered by basaltic areas. $f_{\text{LIP}}$ is the climatic dependence of basaltic rock weathering:

$$f_{\text{LIP}} = k_{\text{bas}} \times \text{run}_j \times e^{-\frac{42300}{T_j}}$$

where $k_{\text{bas}}$ is the ideal gas constant, $T_j$ the mean annual temperature calculated by the climate model for grid element $j$, and run$_j$ is the local mean annual runoff from the climate model. $k_{\text{bas}}$ is a calibration constant (see below). The same formulation is used for the weathering of active volcanic arcs, assuming a basaltic lithology. This simplification maximizes the contribution of arc to the global weathering flux.

The weathering of continental shield rock is calculated using the same formalism:

$$f_{\text{shield}} = \sum_{j=1}^{n_{\text{grid}}} \phi_{\text{shield}} \times \text{area}_j 	imes f_{\text{shield}}$$

with (Oliva et al., 2003):

$$f_{\text{shield}} = k_{\text{shield}} \times \text{run}_j \times e^{-\frac{42300}{T_j}}$$

$k_{\text{shield}}$ and $k_{\text{bas}}$ are calibrated so that the total silicate weathering consumes 6.8 Tmol CO2/yr, with basaltic weathering contributing to 30% of the total for a present day configuration (Gaillardet et al., 1999; Dessert et al., 2003). Carbonate weathering is so fast that it is assumed
to drive the continental runoff to equilibrium with respect to calcite above each continental grid cell, under the calculated CO₂ level.

2.1.1. Strontium budget

The Sr flux released by the weathering of each lithology is assumed to be proportional to the corresponding weathering flux. The strontium isotopic budget has been implemented according to Nardin et al. (2011). The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ($r_{\text{seaw}}$) is calculated according to the following equation:

$$M_{\text{oc}} \frac{dr_{\text{oc}}}{dt} = P_{\text{shield}} \sum_{j=1}^{n_{\text{grid}}} (r_{\text{shield}} \times \text{area}_j \times f_{\text{shield}} \times (r_{\text{oc}} - r_{\text{shield}})) + P_{\text{bas}} \sum_{j=1}^{n_{\text{grid}}} (r_{\text{bas}} \times \text{area}_j \times f_{\text{bas}} \times (r_{\text{oc}} - r_{\text{bas}})) + P_{\text{ARC}} \sum_{j=1}^{n_{\text{grid}}} (r_{\text{ARC}} \times \text{area}_j \times f_{\text{ARC}} \times (r_{\text{oc}} - r_{\text{ARC}})) + P_{\text{carb}} \sum_{j=1}^{n_{\text{grid}}} (r_{\text{carb}} \times \text{area}_j \times f_{\text{carb}} \times (r_{\text{oc}} - r_{\text{carb}})) + M_{\text{MOR}} \times (r_{\text{oc}} - r_{\text{MOR}})$$

where $r_{\text{shield}}, r_{\text{bas}}, r_{\text{ARC}}, r_{\text{carb}}$ and $r_{\text{MOR}}$ are respectively the $^{87}\text{Sr}/^{86}\text{Sr}$ of shield rocks, LIPs, volcanic arcs, carbonate rocks and the mantle value. $M_{\text{MOR}}$ is the strontium exchange flux between seawater and the oceanic crust. $P_{\text{shield}}, P_{\text{bas}}$ and $P_{\text{carb}}$ are proportionality constants that fix the carbon fluxes to the associated strontium fluxes such that the present-day strontium fluxes are identical to the values used by Wallmann (2001). As the seawater strontium isotopic ratio is calculated every 30 to 50 million years, $r_{\text{oc}}$ is assumed to be the multi-million year steady-state value. The left-hand side of Eq. (5) is thus set to 0, and the equation is solved for $r_{\text{oc}}$. $r_{\text{MOR}}$ is set to the mantle value at the age of each simulated time slice. Its evolution with time is calculated as follows (Vidal, 1994):

$$r_{\text{MOR}} = \text{BABI} + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{m} \left(1 - e^{-\lambda_{t}}\right)$$

where $t$ is the age of the considered time slice, with $t = 0$ at the origin of the Earth (age of the Earth fixed at $4.54 \times 10^{9}$ years). BABI is the Basaltic Achondrite Best Initial ratio (0.69897) and $\lambda$ is the $^{87}\text{Rb}$ decay constant ($1.42 \times 10^{-11}$ $\text{yr}^{-1}$). $\left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{m}$ is the $^{87}\text{Rb}/^{86}\text{Sr}$ of the mantle. This ratio is calculated according to the following equation:

$$\left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{m} = 0.2783 \times \left(\frac{\text{Rb}}{\text{Sr}}\right)_{m} \left(9.3485 + \text{BABI}\right)$$

where the Rb/Sr of the mantle is set to 0.025. $r_{\text{shield}}$ is calculated assuming that the continental crust had been mostly weathered by 2.5 Ga:

$$r_{\text{shield}} = \text{BABI} + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{m} \left(1 - e^{-\lambda_{t} \times 2 \times 10^{9}}\right) + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{\text{CC}} \left(1 - e^{-\lambda_{t} \times (1-2 \times 10^{9})}\right)$$

where $\left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_{\text{CC}}$ is the $^{87}\text{Rb}/^{86}\text{Sr}$ of the continental crust. This value is about 10 times larger than the corresponding mantle value (Vidal, 1994). We used it as a calibration constant so that the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater equals 0.7092 under present day climatic conditions (control run).

Finally, $r_{\text{ARC}}$ and $r_{\text{bas}}$ are set to the mantle value at the time of their eruption (but crustal contamination is also tested below in the case of LIPs). $r_{\text{carb}}$ is set to 0.706 which is close to the seawater value before 825 Ma (Fig. 1). The riverine $^{87}\text{Sr}/^{86}\text{Sr}$ is calculated as the weighted average of the Sr flux originating from the weathering of each lithology.

2.2. Boundary conditions: reconstructing the Neoproterozoic world

In order to study the effect of paleogeography and lithology on climate and the Sr cycle, we first generated a series of paleogeographic maps spanning the breakup of the supercontinent Rodinia, based on the reconstructions of Li et al. (2013). We then overlaid a simple lithological layer onto these maps, in which young juvenile crust (i.e. basalt) is distinguished from old continental crust (i.e. granite).

The configuration of Rodinia from its assembly to its complete disintegration is still highly debated (Li et al., 2008). If the central position of Laurentia within the supercontinent is well established (Bond et al., 1984), several competing models exist for the arrangement of cratons that surround it (e.g. Dalziel, 1991; Hoffman, 1991; Moores, 1991; Li et al., 1995; Burrett and Berry, 2000; Sears and Price, 2000; Wingate et al., 2002; Li et al., 2008; Pisarevsky et al., 2008). The paleogeographies proposed by Li et al. (2013) have been chosen for this study because they are constrained by both paleomagnetic data and the correlation of geological features (orogens, sedimentary terranes, basement provinces, continental and passive margins, or mantle plume and magmatic records). Using these paleogeographies, we simulate seven time slices: 825 Ma, 780 Ma, 720 Ma, 680 Ma, 635 Ma, 580 Ma, and 540 Ma (Fig. 2).

Continental arcs were included on all active margins following Li et al. (2013) (Fig. 2). Because the surficial extent of arcs on the margins of Rodinia is totally unconstrained, we set the ratio (arc surfaces/total continental surface) to the present day value of 1.6. This number was obtained by combining a high-resolution global lithological map (GLiM) (Hartmann and Moosdorf, 2002) and a 0.5° × 0.5° digital elevation model. We select topographic zones characterized by active magmatism linked to an active subduction to calculate the surface of the active continental margins at present day. We found that the total surface of island arcs and continental arcs displaying active magmatism is respectively 1 and 1.5 Mkm² (1.6% of the total emerged continents). Going into the past, a fraction of each continental grid element located along active margins (according to the reconstruction of Li et al. (2013)) is covered by volcanic arcs. This fraction depends on the simulated time slice, and is set so that the total volcanic arc area reaches 1.6% of the total continental surfaces (i.e., total arc length is fixed). The remaining surface of the grid cell is filled with granites and carbonates.

Multiple large LIPs were emplaced onto Rodinia in the early Neoproterozoic and these are included in our paleogeographic reconstructions. A total of seven LIPs were included in the 825 Ma paleogeography, the oldest of which was erupted at 1100 Ma. Younger LIPs dated at ca. 780, 720, and 580 Ma were added to younger paleogeographies for a total of thirteen different LIPs by 540 Ma (Ernst et al., 2008). It is difficult to assess the original extent for flood basalts, because only remnants of these initially widespread magmatic events are still visible (Ernst et al., 2008). Likewise, the rates at which these LIPs eroded are poorly constrained. Here we used estimates for the original size from Ernst et al. (2008), which were based on both extant surficial exposures of continental flood basalts (CFBs) and the deeper network of these LIPs, represented by giant dike swarms, sill provinces and layered intrusions. To account for their progressive destruction with time (by weathering, erosion, continental accretion or subduction), we allowed their surficial extents to decrease exponentially as a function of their age. Based on available reconstructions of the initial size of five major LIPs, on their age, and on their present day extent (Courtillot and Renne, 2003; Ernst et al., 2013), we calculated half-lives for this exponential decay ranging from 90 (Deccan Traps) to more than 400 million years (Parana–Etendeka), with the remaining three clustering around 100 million years (Table 1). The number of samples is by far too low to perform any statistical analysis, but it provides a useful first-order model appropriate to the time resolution of our study. To test the sensitivity of the chosen decay constants, we explore the geochemical consequences of LIP half-lives of 50, 70, 90, 110, 130, and 150 Myr.

2.3. The Neoproterozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$ signal

For the record of Neoproterozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$, we used the compilation from Halverson et al. (2007), with an updated age model from Cox et al. (2016) and new data from Bold et al. (2016) (Fig. 3).
The model outputs are compared to those data. As already mentioned, we explore the long-term evolution in response to paleogeography and first order lithological changes at a characteristic timescale of several tens of million years. At this timescale, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ can be qualitatively described as follows: low values between 0.705 and 0.706 are typical of the period from 1050 to 825 Ma. A rise to values near 0.707 occurs from about 825 to 780 Ma, which follows by a plateau around 0.7067 until 720 Ma. From 720 to about 660 Ma, there is a long gap without data corresponding to the long duration of the Cryogenian glaciation (Rooney et al., 2014, 2015). At 660 Ma $^{87}\text{Sr}/^{86}\text{Sr}$ values were nearly identical to those immediately preceding glaciation but rise abruptly to $>0.072$ during the short (~15 m.y.) interglacial interval. Another sharp rise occurs following the Marinoan glaciation (ca. 635 Ma), followed by stabilization near 0.708, which precedes a final increase to values near 0.7085 from 580 to 540 Ma.

3. Results
3.1. Calibration and baseline simulation

We first calibrated the strontium isotopic cycle using the present day continental configuration under 280 ppm of atmospheric CO$_2$ and seawater $^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$ (Veizer et al., 1999). This configuration includes the location of LIPs and volcanic arcs and accounts for elevated $^{87}\text{Sr}/^{86}\text{Sr}$ in the Himalayan range. We then performed a first Neoproterozoic simulation (referred to as ‘radioactive decay’) for a

![Fig. 2. The digitized continental configurations used as boundary conditions of the GEOCLIM model (Li et al., 2013). In yellow, the location of continental arcs, in green the location of large igneous provinces, and in red the Pan-African orogen. AN: Arabo-Nubian; GM: Ganghil-Mayubian; SW: South West USA; W: Warakurna; WG: Willouran-Gairdner; SC: South China (merges 4 LIPs); B: Bir El Khzaim; F: Franklin; G: Gunbarrel (Ernst et al., 2008).](image)

### Table 1

<table>
<thead>
<tr>
<th>LIP</th>
<th>Age (Ma)</th>
<th>Initial surface ($10^6$ km$^2$)</th>
<th>Present day surface ($10^6$ km$^2$)</th>
<th>$t_0$ (Myr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emeishan</td>
<td>261–251</td>
<td>3.5</td>
<td>0.5</td>
<td>129–134</td>
</tr>
<tr>
<td>Siberian</td>
<td>254–248</td>
<td>4</td>
<td>0.4</td>
<td>108–110</td>
</tr>
<tr>
<td>Parana-Etendeeka</td>
<td>138–125</td>
<td>2</td>
<td>1.5</td>
<td>425–480</td>
</tr>
<tr>
<td>Deccan</td>
<td>67–60</td>
<td>1</td>
<td>0.5</td>
<td>87–97</td>
</tr>
<tr>
<td>Ethiopian</td>
<td>31–14</td>
<td>0.8</td>
<td>0.7</td>
<td>105–232</td>
</tr>
</tbody>
</table>
paleogeography with no basaltic surfaces. This simulation provides a baseline seawater $^{87}\text{Sr}/^{86}\text{Sr}$ evolution for the Neoproterozoic based solely on changing paleogeography (Fig. 4). As the degassing of the solid Earth is held constant, the total silicate rock weathering is the same for each time slice. The associated riverine flux of Sr is thus constant through the whole investigated time window. The rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is fully driven by the radioactive decay of the $^{87}\text{Rb}$ in silicate rocks. Fluctuations in carbonate weathering from one continental configuration to the other are responsible for second order fluctuations in the calculated seawater $^{87}\text{Sr}/^{86}\text{Sr}$.

3.2. The middle Neoproterozoic time window (825–635 Ma)

The following set of simulations account for the weathering of young volcanic arcs and for the weathering of successively erupted LIPs, with a surficial decay constant ($t_0$) ranging from 50 to 150 Myr. When the fastest decay constant is assumed (i.e., $t_0 = 50$, which means that half of the surface of each LIP disappears 50 million years after the eruption), the calculated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ increases almost monotonically from 0.7067 at 825 Ma to 0.708 at 540 Ma (Fig. 4). Two small inflections are nevertheless predicted. The first one occurs between 780 and 680 Ma and the second after 635 Ma. If $t_0$ increases, those inflections are amplified. When $t_0$ is set to the maximum value of 150 Myr, the calculated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ stays nearly constant between 780 and 680 Ma. These results agree with the available data (Fig. 4) in showing a middle Neoproterozoic plateau in the $^{87}\text{Sr}/^{86}\text{Sr}$.

As the simulation performed with $t_0 = 150$ Myr yields the best results for the time interval from 825 to 635 Ma, we restrict the following discussion to this model run. We identify two main culprits for the rapid increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ stagnation between 780 and 680 Ma (Fig. 6). The first, the eruption of the Franklin LIP at ca. 730 Ma (Ernst et al., 2008), delivers the high radiogenic strontium due to its redistribution into more easily weatherable minerals during high grade metamorphism in the cores of large mountain belts (Edmond, 1992). The second, the eruption of the Arabian–Nubian LIP, erupted around 850 Ma (Ernst et al., 2008), increases from 720 and 680 Ma. It contributes to the total Sr flux coming from the continental weathering of silicates, which reaches more than 5% at 680 Ma, helping to maintain constant seawater strontium isotopic ratio. This intense weathering occurs when the Arabian–Nubian LIP straddles 30° S, just north of the modeled divergence zone and the corresponding low runoff area (Figs. 5 and 7). The other eleven LIP provinces mapped on our paleogeographic reconstructions play only a minor role from 825 to 680 Ma (Fig. 6).

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At 635 Ma, the Sahara metacraton (to which the ANS had by then accreted; Johnson et al., 2011) does not move significantly, but the divergence zone expands towards the equator and above the Arabian–Nubian LIP. As a consequence, its contribution to global weathering collapses from 5% to 0% from 680 to 635 Ma as runoff falls to virtually nil (Figs. 6 and 7). Combined with the southward drift of the Franklin LIP, the overall decrease in LIP weathering at 635 Ma explains the marked rise in the riverine and seawater $^{87}\text{Sr}/^{86}\text{Sr}$, consistent with the $^{87}\text{Sr}/^{86}\text{Sr}$ record spanning the Cryogenian (Fig. 3).

3.3. The Ediacaran time window (635–540 Ma)

Despite broad agreement between the $t_0 = 150$ Ma simulation and the available strontium data for the 825–635 Ma time window, model output and data diverge at 580 and 540 Ma. The model predicts a second plateau until 580 Ma followed by an increase at 540 Ma (Fig. 4). This second Ediacaran plateau in the model is due to South China. Located at 50° N at 635 Ma and carrying the remnants of the Guibei, Kangding and Shaba LIPs, the South China craton enters the intertropical convergence zone (ITCZ) at 580 Ma (Li et al., 2013) (Fig. 5). The calculated weathering rates of these three LIPs rapidly rise, accounting for 5% of the total silicate weathering at 580 Ma, and 6.5% at 540 Ma (Fig. 6).

The most important paleogeographic feature of the Ediacaran is the uplift of the Pan-African orogenies, by which the megacraton of Gondwana accreted. Derry et al. (1989) first suggested that the silicate rocks exposed in the Pan-African orogenic belts might have been highly radiogenic, similar to the Himalayan crystalline rocks, which are a rich source of radiogenic strontium due to its redistribution into more easily weathered minerals during high grade metamorphism in the cores of large mountain belts (Edmond, 1992). We tested this possibility by setting the $^{87}\text{Sr}/^{86}\text{Sr}$ of silicate rocks in uplifted area to higher values than the mean continental crust $^{87}\text{Sr}/^{86}\text{Sr}$. Several values have been tested and we found that the best fit with the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is reached when it is set to an average value of 0.730 (compared to the calculated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is 0.7141). By adopting this value, the average $^{87}\text{Sr}/^{86}\text{Sr}$ of the runoff draining Pan African orogens is calculated to be 0.7183, with a maximum of 0.726. Fluctuations in the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of run-off are then driven by the relative contribution of carbonate versus silicate weathering to the Sr flux exported from the range. The contribution of each lithology is driven by the calculated runoff and temperature for each grid cell belonging to the range.
average value of 0.7183 is below the annual mean isotopic ratio of the Ganges–Brahmaputra River of 0.7295 (Galy et al., 2002). The modest and geologically reasonable adjustment yields a much-improved fit between our model and Ediacaran seawater isotopic compositions, particularly at 580 Ma (Fig. 8). The calculated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ at 540 Ma stays below the observed range. Renewed weathering of low radiogenic rocks, related to the drifting of older LIPs (South China, Warakurna, and Willouran-Gairdner) into the equatorial convergence zone, reduces the impact of the Pan-African orogens on the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in the model (Figs. 5 and 8).

3.4. Coeval evolution of atmospheric CO2 and climate

The simulation adjusted to most closely match the strontium isotope data predicts an overall decrease in atmospheric CO2 levels through most of the Neoproterozoic (Fig. 9). CO2 reaches a maximum at 780 Ma (close to 80 times the pre-industrial atmospheric level, or 80 PAL) and a minimum at 580 Ma (4.6 PAL). The evolution in CO2 is paced by the demise of the Rodinia supercontinent, consistent with earlier results (Donnadieu et al., 2004). This coupling between the geography of a splintering supercontinent and atmospheric CO2 levels
is mainly the result of the extent and distribution of deserts. The continents were largely covered in deserts at 780 Ma, inhibiting runoff and silicate weathering (Fig. 7). Such vast aridity leads to higher CO$_2$ in order to maintain the global balance between volcanic outgassing and CO$_2$ consumption by weathering. Subsequent disintegration of Rodinia increases the runoff and enhances silicate weathering, causing CO$_2$ to decrease. By 580 Ma, only small continental surfaces are located in the arid climatic belts (tropical divergence zones). As a result, the runoff value is maximal and atmospheric CO$_2$ reaches its lowest value.

A more nuanced history emerges from annual average continental temperatures (Fig. 10). Following the very high temperatures at 780 Ma (around 27 °C), the model predicts a first major cooling event between 780 and 720 Ma (4 °C decrease). A second drop in continental temperature is predicted between 680 and 635 Ma (7 °C decrease) (Figs. 10 and 11). Cooling between 780 and 720 Ma is due in part to the break-up of Rodinia and in part to the enhanced contribution of basaltic weathering of the Franklin and Arabian/Nubian LIPs. Continued cooling between 680 and 635 Ma occurs in spite of a decrease in basalt weathering because this effect is counteracted by a 40% increase in runoff in the equatorial area due to a more dispersed, tropical paleogeography (Fig. 7). This increased runoff, concentrated on Laurentia, Siberia, and the North China craton, boosts CO$_2$ consumption by continental silicate weathering. Following this major cooling, the mean annual temperature of the continents stays roughly constant at 15 to 17 °C over ensuing (Ediacaran) time slices, despite a continuous decrease in CO$_2$.

These simulations, which are based on an updated and more comprehensive paleogeographic reconstructions, validate previous models.


4.1. Solid Earth degassing

Although continental drift appears to exert first order control on the evolution of Earth’s climate, other processes indubitably played a role. It has recently been suggested that continental arc volcanism was at a minimum during the Cryogenian (McKenzie et al., 2016), based on the age distribution of a compilation of detrital zircons. The link between the age distribution of zircon formed predominantly in granite and the effective solid Earth degassing of CO$_2$ into the exospheric system is yet to be quantified, and the temporal resolution of the McKenzie et al. (2016) compilation for the Neoproterozoic is low (just one point each for the Cryogenian and Ediacaran periods). But this raises the potential importance of variable solid Earth CO$_2$ degassing rates, which are otherwise fixed in our model simulations. As a very first order test, we ran additional simulations in order to test the hypotheses that variable degassing rates exerted an important control on Neoproterozoic climate. For time slices prior to 600 Ma, we fixed the global solid Earth degassing at 60% of its present day value. For the two younger time slices (580 and 540 Ma), we fix the global solid Earth degassing to the present day value multiplied by a factor of 1.4. This simplified secular degassing history broadly mimics the cumulative proportion of young zircons reconstructed for the last 720 million years.

The most conspicuous consequence of the prescribed variable degassing model simulation is a leveling of the CO$_2$ fluctuations, which in this run range from 10 to 30 times the pre-industrial level (Fig. 12). CO$_2$ levels decrease prior to 600 Ma and increase after 600 Ma, compared to the previous runs, in direct response to the degassing scenario. Consequently, the mean annual temperature of the Ediacaran continental surfaces is now above the temperatures of all the Cryogenian simulations, reaching 20 °C (Figs. 13 and 14). Responding to the sharp decrease in solid Earth degassing, the Cryogenian continental temperatures fall by about 10 °C. But the general trend remains unchanged: the paleogeographic forcing coupled to the changes in lithology forces temperatures to decrease by 15 °C from 780 Ma to the 635 Ma minima of 6 °C.

Although variable degassing as predicted by the McKenzie et al. (2016) model would result in average cooler Cryogenian temperatures, significant cooling leading into the Cryogenian glaciation must still be accounted for by paleogeographic (sink) rather than source controls on CO$_2$ (Fig. 13). Furthermore, the variable degassing model appears to be at odds with middle Ediacaran glaciation. Consequently, although variable degassing could have played a role in modulating Neoproterozoic climate, it is clear that paleography exerted an equal or greater role. Interestingly, the calculated seawater $^{87}$Sr/$^{86}$Sr remains virtually unchanged despite variable degassing, reinforcing the fact that the strontium isotopic record cannot be used as a proxy for either CO$_2$ or climate. This absence of sensitivity in $^{87}$Sr/$^{86}$Sr to variable degassing rates is related to the silicate negative feedback loop embedded in the model: if the degassing increases, the magmatic processes producing low radiogenic strontium become more active, but the rise in CO$_2$ and associated climate change forces the continental weathering to increase, enhancing the delivery of radiogenic strontium to seawater, strongly dampening the changes in seawater $^{87}$Sr/$^{86}$Sr (Goddéris and François, 1996).

4.2. True polar wander

The continental configurations used in our model assume a true polar wander event (90° rotation of Rodinia) between the 825 and 780 Ma (Li et al., 2013). The comparison of the 825 and 780 Ma simulations thus serves as an approximate sensitivity test of the Earth system due to a single true polar wander event. In these paleogeographies, Rodinia is entirely located in the northern hemisphere before the rotation, and mostly in the southern hemisphere after the rotation (Fig. 2). As a result, average continental runoff is higher at 825 Ma compared to 780 Ma. Indeed, the equatorial location of Rodinia at 780 Ma intercepts the southern and northern divergence zones at 780 Ma, while the 825 Ma configuration only intercepts the northern zone (Fig. 7). Continental weatherability is thus higher at 825 Ma than at 780 Ma, and the calculated CO$_2$ at 825 Ma is about two times lower.
than at 780 Ma (Fig. 9). This behavior is not intuitive. A predominantly high-latitude location of continental masses should inhibit weathering because of low temperatures, allowing CO₂ to rise (Goddéris et al., 2014). But in the case of a supercontinent, aridity dominates over latitude in controlling silicate weathering. This result illustrates the complex interaction between continental location and continental area and the need for global climate simulations to determine the dominant mechanisms controlling silicate weathering and atmospheric CO₂ for specific paleogeographic reconstructions.

As for the strontium isotopic cycle, the relative contribution of basaltic rock weathering to the Sr flux to the ocean is about constant between 825 and 780 Ma. The resulting seawater ⁸⁷Sr/⁸⁶Sr is thus about the same. Conversely, the ⁸⁷Sr/⁸⁶Sr compilation displays a lower value at 825 Ma that is not resolved by the current modeling. This discrepancy reveals the need for future work, including using seawater strontium isotopic ratios as a test of the true polar wander hypothesis.

4.3. Total continental surface

The late Neoproterozoic paleogeographies (580 and 540 Ma) are characterized by intense runoff. The dispersed continental configuration and the lack of continents in the tropical divergence zones allow the

Fig. 11. Continental annual temperatures calculated for the 7 simulated time slices at steady-state CO₂ calculated by the "150 Ma" run of Fig. 9.

Fig. 12. Testing the role of variable solid Earth degassing on the evolution of Neoproterozoic climate. The dashed line represents the evolution of atmospheric CO₂ calculated assuming a variable degassing rate, while the solid line depicts the results for the constant degassing model.
development of relatively humid conditions over large areas. A third geographic factor might also contribute to this climate: the total continental surface. From 825 to 635 Ma, the total continental size fluctuates between 140 and 150 Mkm$^2$ based on the paleogeographic reconstructions used. But this surface decreases to 103 Mkm$^2$ at 580 Ma, and to 110 Mkm$^2$ at 540 Ma, which is in part an artifact of the digitization of the maps and is not geologically accurate. Because small continental sizes promote humidity, they may overestimate the global runoff. We might expect that CO$_2$ will increase with the average size of continents. But it is difficult to predict the response of the seawater $^{87}$Sr/$^{86}$Sr to continental size, because the pattern of rainfall will also be affected, impacting on the relative contribution of each lithology to the total continental strontium discharge. Testing the response of the Earth system to the size of the continents is beyond the scope of this contribution, but we here emphasize the deep dependence of models to the reliability of the paleogeographic maps.

4.4. Snowball Earth glaciations

We do not explicitly examine the role of snowball Earth events on the seawater $^{87}$Sr/$^{86}$Sr in our simulations because the objective of this
contribution is to explore the long-term Sr isotopic record of the Neoproterozoic in response to continental drift and changes in lithology. Since the interval between each simulated time slice is between 40 and 60 Myr, we did not consider the impact of shorter-term processes such as enhanced weathering during the recover from snowball glaciations. Nevertheless, new geochronological results have revised the duration of the Sturtian glaciation to be much longer than previously thought (i.e. 57 Myr, from ca. 717 to 660 Ma; Rooney et al., 2014, 2015). These new ages call into question the significance of the 680 Ma simulation, which would have been within the early Cryogenian (Sturtian) snowball glaciation. However, our model is not designed to capture the dynamics of a snowball glaciation, such as whether this event was a long-lived hard snowball or a succession of glaciation advances and retreats (Spence et al., 2016). In this regard, the precise timing of the reconstruction relative to snowball glaciation is immaterial; it reflects the Earth system at steady-state when only paleogeography and lithology are accounted for.

The impact of the snowball events on the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ evolution is yet to be quantified. Bold et al. (2016) suggest that the brief respite observed at 660 and 635 Ma are the consequence of the intense weathering occurring during the snowball melting phase. However, Le Hir et al. (2009) showed that continental silicate weathering cannot exceed about 3 times its present day value (in the best case) during the melting phase, assuming 0.1 bar of CO2 in the atmosphere because runoff levels off when the total amount of latent energy used for evaporation approaches the solar energy input. Furthermore, the peak in intense weathering conditions should persist no longer than ca. 10 kyr (Le Hir et al., 2009). This peak should produce a peak in seawater $^{87}\text{Sr}/^{86}\text{Sr}$. But once the pool of readily dissolved rock flour residual from glaciation is dissolved, seawaters $^{87}\text{Sr}/^{86}\text{Sr}$ should come back to its pre-glacial level within about 10 million years (corrected for $^{87}\text{Rb}$ decay), unless after both glacial scouring and intense weathering, the lithology of the continents had been significantly modified. For example, Cox et al. (2016) argued that snowball glaciation would likely have accelerated the removal of LIPs from the continents, which would have influenced long-term strontium cycling.

### 4.5. Crustal contamination

The average $^{87}\text{Sr}/^{86}\text{Sr}$ of LIPs is often contaminated by radiogenic crustal sources. The above simulations have been carried out assuming that the $^{87}\text{Sr}/^{86}\text{Sr}$ of LIPs was equal to the mantle value, maximizing the impact of their weathering on the seawater $^{87}\text{Sr}/^{86}\text{Sr}$. We present two additional simulations to explore the impact of a crustal contamination on the seawater isotopic signal. Data are sparse, but the initial isotopic ratio of the Franklin province has been calculated at 0.7046 from the data of Shellnutt et al. (2004). As a first test, we re-run the “150 Ma” simulation, assuming that all LIPs considered in this study display the same crustal contamination as the Franklin LIP (simulation labeled “Contamination1” in Fig. 15). The second test is based on the observation that the best documented continental flood basalts in the GEOROC database (all younger than 300 Myr) display an average $^{87}\text{Sr}/^{86}\text{Sr}$ that is ~0.004 higher than the mantle at the time of their onset. We assume this same enrichment for all end Proterozoic LIPs in the simulation labeled “Contamination2” (Fig. 15).

As shown in Fig. 15, the impact of crustal contamination on the calculated seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is resolvable, but does not change the general pattern.

### 5. Conclusions

In summary, our model results suggest the following scenario for the long-term seawater $^{87}\text{Sr}/^{86}\text{Sr}$ evolution. Between 825 and 635 Ma, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is driven by the progressive enrichment in $^{87}\text{Sr}$ in continental rocks due to radiogenic ingrowth. However, this gradual trend is modulated by the weathering of LIPs, which were unusually abundant during this time interval. The release of unradiogenic Sr by LIP weathering is a function of the size, age, and most importantly, the paleogeographic location of the LIPs. Acceleration of LIP-weathering between 780 and 680 Ma stabilized seawater $^{87}\text{Sr}/^{86}\text{Sr}$ over the same time window. Conversely, the collapse of the LIP weathering flux after 680 Ma driven by continental drift allows the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ to rise again. At the resolution of our modeling, the effect of the Pan African orogeny on the global isotopic strontium cycle is maximal at ca. 580 Ma. Enrichment in $^{87}\text{Sr}$ of the igneous rocks exposed in the mountain ranges (mean value of 0.740; Edmond, 1992) is required to simulate the seawater record.

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### References


