Land plants decreased, rather than increased, weathering rates over the Phanerozoic

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Paleozoic pCO_2 and $\delta^{13}C$ values

For the averaging described below we bin the pCO_2 and carbonate $\delta^{13}C$ datasets based on the following time periods:

- Late Cambrian to Early Ordovician: 500 to 470 Ma
- Early Ordovician to Devonian: 470 to 360 Ma
- Mississippian: 360 to 323 Ma
- Pennsylvanian: 323 to 299 Ma
- Permian: 299 to 252 Ma

In Figure 2 we present timeseries of the central estimate and 68% confidence intervals from a recent proxy compilation of atmospheric pCO_2 (Foster et al., 2017) and GEOCARBSULF modeling of atmospheric pCO_2 (Schachat et al., 2018; Royer et al., 2014; Berner, 2006). This data is subsequently discussed in the text and averaged in Figure 3. Note that in Figures 2 and 3 we plot normalized pCO_2 values relative to preindustrial (280 ppm).

Foster et al. (2017) presented an updated compilation since 420 Ma of atmospheric pCO_2 data by applying a consistent set of criteria to filter and renormalize all Phanerozoic pCO_2 estimates. During the Paleozoic, pCO₂ are exclusively based on leaf stomata and pedogenic carbonate δ^{13} C reconstructions, recalculated using consistent criteria based on the literature (see Methods of Foster et al. (2017); Beerling and Royer, 2002; Breecker et al., 2010). Foster et al. (2017) provided a LOESS fitting curve, including quantifying uncertainty using a Monte Carlo approach outputted at 0.5 Myr timesteps. Recent modeling by Schachat et al. (2018) updated the input datasets used by Royer et al. (2014) in the GEOCARBSULF modeling estimates of atmospheric pCO_2 and pO_2 outputted at 10 Myr timesteps. Schachat et al. (2018) updated the carbon, sulfur and strontium isotope input datasets. Here we use the 'bulk rock' carbonate $\delta^{13}C$ dataset and the resultant output, since we use the readily available 'bulk rock' $\delta^{13}C$ dataset in the text (next paragraph). We note, however, that this decision does not influence the observed interpretation of long-term increases in carbonate δ^{13} C over the Paleozoic. In Figure 3, the vertical lines are the average pCO_2 values calculated for the Late Cambrian to Early Ordovician (2769 ppm); Early Ordovician to Devonian (1633 ppm); Mississippian (423 ppm); Pennsylvanian (355 ppm) and the Permian (535 ppm). To calculate these averages, we use the proxy dataset (Foster et al., 2017) except for the Late Cambrian to Early Ordovician and Early Ordovician to Devonian due to the lack of data beyond 420 Ma. We note that for the Early

Ordovician to Devonian period (470 to 360 Ma) where proxy data do exist the average compares favorably to the GEOCARBSULF results (GEOCARBSULF $pCO_2 = 1633$ ppm vs. proxy data average from 259 to 419.5 Ma = 1327 ppm).

In the text, we also discuss the marine carbonate δ^{13} C record compiled by Saltzman and Thomas (2012) and utilized by Bachan et al. (2017) to analyze long and short wavelength trends in marine carbonate δ^{13} C over the Phanerozoic. While not used quantitatively in our analysis, we do calculate average Late Cambrian to Early Ordovician, Mississippian and Permian δ^{13} C values as representing the long wavelength increases over the Paleozoic (Bachan et al., 2017). Longterm increases in δ^{13} C represent increased organic carbon burial relative to carbonate burial in the exogenic carbon cycle, though this trend may also be driven by other burial processes such as ocean-crust carbonate precipitation and changes in the volcanic δ^{13} C value (for further details see Hayes and Walbauer (2006)).

Silicate weathering feedback and imbalance calculations

In Figures 1 and 3, we use a generic version of the silicate weathering feedback relating RCO₂ to changes in silicate weathering (and the carbon input flux at a given time period). The most general form of the feedback equation that has been used extensively in carbon cycle models is a power-law equation (Uchikawa and Zeebe, 2008; Caves et al., 2016; Winnick and Maher, 2018):

$$F_{sil} = F_{volc,eq} [RCO_2]^n$$
(1),

where F_{sil} is the normalized silicate weathering rate, $F_{volc,eq}$ is an equilibrium (modern) volcanic degassing rate or carbon input flux, [RCO₂] is atmospheric *p*CO₂ normalized to preindustrial (modern *p*CO₂ = 280 ppm), and n is the reaction order term. Note that since the carbon input flux must be balanced on long timescales by silicate weathering fluxes (Berner and Caldeira, 1997) the y-axis on Figure 3 represents inputs or outputs at a given time period.

Previous work, starting with the seminal work by Walker et al. (1981) has constrained or arbitrarily specified n to range between 0.2 to 1, though typical carbon cycle models range from 0.2 to 0.6, where 0.2 represents a weak feedback and 0.6 represents a strong feedback (see discussion in Caves et al., 2016; Berner, 2006; Uchikawa and Zeebe, 2008). At present, while it is clear that the rise of land plants likely increased the silicate weathering feedback strength through multiple mechanisms (e.g., Berner, 1992; Drever, 1994; Ibarra et al., 2019), it is not yet

clear how much stronger the silicate weathering feedback was or how rapidly it may have strengthened. Thus, for this work we do not make quantitative predictions using this framework. Within this theoretical framework, as presented, we knowingly neglect to provide a mechanism to link Ca^{2+} concentrations in the global ocean to weathering and long-term CO_2 drawdown. This pursuit is beyond the scope of this paper.

In Figure 1, we calculate the drawdown of pCO_2 given initial pCO_2 values and feedback strength for 1%, 5% and 25% excess silicate weathering. This numerical experiment was originally presented by Berner and Caldeira (1997) and we use the imbalance calculations presented in Zeebe and Caldeira (2008) and Caves et al. (2016) to carry out our calculations. Here, based on previous work, we briefly derive Equation 1 in the main text and describe the assumptions used in our calculations. Starting with two mass balance equations of the exogenic inventories of carbon (M_C) and alkalinity (M_A) (Kump and Arthur, 1999; Zeebe and Wolf-Gladrow, 2001; Zeebe and Caldeira, 2008; Caves et al., 2016):

$$\frac{dM_c}{dt} = F_{wcarb} - F_{bcarb} + F_{volc} + F_{worg} - F_{borg}$$
(2),
and
$$\frac{dM_A}{dt} = 2F_{wcarb} - 2F_{bcarb} + 2F_{sil}$$
(3),

where F_{volc} is the volcanic flux, F_{worg} and F_{borg} are the weathering and burial of organic matter, F_{wcarb} and F_{bcarb} are the weathering and burial of carbonates, and F_{sil} is the silicate weathering flux. (Note that to simplify our formulation we do not include the oxidative weathering and burial of pyrite in these calculations; e.g., Torres et al. (2014); Caves Rugenstein et al., (2019)). As outlined by Caves et al. (2016) subtracting equation 3 from equation 2 to calculate the imbalance (I) gives the equation presented in the main text:

$$I = \frac{dM_{C}}{dt} - 0.5 \frac{dM_{A}}{dt} = F_{volc} + F_{worg} - F_{borg} - F_{sil}$$
(4; Equation 1 main text).

In Figure 1, we impose weathering imbalances of 1%, 5% and 25% using a simplified numerical forward model of the carbon cycle (following Caves Rugenstein et al. (2019) and Kump and Arthur (1999)) using a backward difference approach at 10,000-year timesteps assuming that the ocean and atmosphere are in equilibrium. All initial reservoirs (ocean volume, salinity, calcium concentration, and initial inorganic carbon reservoir of the ocean and atmosphere) and fluxes (variables in above equations) are taken from Caves Rugenstein et al. (2019), initial pCO_2 is set to either 280 ppm or 2800 ppm (following Berner and Caldeira, 1997) and initial pH is set to 7.9.

At each timestep the mass balance of the surface carbon reservoir is calculated using a silicate weathering flux with different feedback strengths (n = 0.2 for initial pCO_2 of 2800 ppm or 0.6 for initial pCO_2 of 280 ppm; next paragraph) multiplied by different imbalance values. The new (lower) pCO_2 value for that timestep is then calculated by speciating the carbonate system using the 'carb' function in the *seacarb 3.2.12* R package (Gattuso et al., 2019). Note that the results of this simple model with 25% excess silicate weathering (red line and black solid line in Figure 1) are functionally equivalent to the curves originally presented in Berner and Caldeira (1997).

Changing the feedback strength from 0.2 to 0.6 while decreasing atmospheric pCO_2 over the Paleozoic appears to necessitate minimal large changes in volcanic degassing. Using the average pCO_2 described above and a transition from a weak to strong silicate weathering feedback results in minimal required changes in carbon input flux into the system (~±15%). If land plants did not strengthen the silicate weathering feedback this framework would suggest large (2- to 5-fold) changes in volcanic degassing during the Paleozoic (see also caption to Figure 3).

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