



## RESEARCH ARTICLE

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## Changing tectonic controls on the long-term carbon cycle from Mesozoic to present

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## Key Points:

- We construct a forward model of granite, basalt, and seafloor weathering
- High Mesozoic CO<sub>2</sub> degassing countered by basalt and seafloor weathering
- Three distinct weathering regimes identified during 230 Ma to present

## Supporting Information:

- LIP table
- BA\_forcing\_data
- Supporting information

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**Abstract** Tectonic drivers of degassing and weathering processes are key long-term controls on atmospheric CO<sub>2</sub>. However, there is considerable debate over the changing relative importance of different carbon sources and sinks. Existing geochemical models have tended to rely on indirect methods to derive tectonic drivers, such as inversion of the seawater <sup>87</sup>Sr/<sup>86</sup>Sr curve to estimate uplift or continental basalt area. Here we use improving geologic data to update the representation of tectonic drivers in the COPSE biogeochemical model. The resulting model distinguishes CO<sub>2</sub> sinks from terrestrial granite weathering, total basalt weathering, and seafloor alteration. It also distinguishes CO<sub>2</sub> sources from subduction zone metamorphism and from igneous intrusions. We reconstruct terrestrial basaltic area from data on the extent of large igneous provinces and use their volume to estimate their contribution to degassing. We adopt a recently published reconstruction of subduction-related degassing, and relate seafloor weathering to ocean crust creation rate. Revised degassing alone tends to produce unrealistically high CO<sub>2</sub>, but this is counteracted by the inclusion of seafloor alteration and global basalt weathering, producing a good overall fit to Mesozoic-Cenozoic proxy CO<sub>2</sub> estimates and a good fit to <sup>87</sup>Sr/<sup>86</sup>Sr data. The model predicts that seafloor alteration and terrestrial weathering made similar contributions to CO<sub>2</sub> removal through the Triassic and Jurassic, after which terrestrial weathering increased and seafloor weathering declined. We predict that basalts made a greater contribution to silicate weathering than granites through the Mesozoic, before the contribution of basalt weathering declined over the Cenozoic due to decreasing global basaltic area.

## 1. Introduction

Atmospheric CO<sub>2</sub> is thought to have fluctuated considerably over geologic time, with solar, biological and tectonic forcing factors all having an effect. Models of the long-term carbon cycle aim to capture these various drivers, alongside the key processes, in order to predict past changes in atmospheric CO<sub>2</sub> [Arvidson *et al.*, 2006; Bergman *et al.*, 2004; Berner, 1991, 2006a]. Model predictions can be tested against CO<sub>2</sub> proxy estimates [Park and Royer, 2011], which become more frequent toward the present day. During most of the Mesozoic and Cenozoic the climate has been warmer than today, with proxy estimates suggesting generally elevated atmospheric CO<sub>2</sub>. Existing models suggest tectonic factors were a key driver of CO<sub>2</sub> fluctuations during this interval [Berner, 2006b; Li and Elderfield, 2013], with increased degassing input producing higher atmospheric CO<sub>2</sub> during the Mesozoic, and then a combination of declining degassing and increasing weatherability of the land surface (due in particular to mountain building [Raymo and Ruddiman, 1992]) causing CO<sub>2</sub> to decline during the Cenozoic. However, the pattern and magnitude of variation in tectonic forcing factors is uncertain, and correspondingly there is considerable disagreement over the varying contribution of different CO<sub>2</sub> source and sink processes over Mesozoic-Cenozoic time.

Existing models generally use indirect methods to estimate variations in tectonic forcing factors such as degassing rates and the supply of easily weathered volcanic rocks [Berner, 2006b]. However, recent advances now make it possible to estimate these variations in forcing more directly from geological and geophysical data. Notably, Van Der Meer *et al.* [2014] have produced a reconstruction of combined arc and ridge CO<sub>2</sub> degassing over the last 230 million years based on the length of subduction zones reconstructed from geophysical “imaging” of subducted plates. Compared to earlier work, the result is markedly increased degassing through much of the Mesozoic. The authors use their new degassing function to force a version of the GEOCARBSULF geochemical model [Berner, 2006a]. They find that bringing CO<sub>2</sub> predictions back into agreement with proxy data for the Mesozoic is possible but requires an enhancement of the CO<sub>2</sub> sink via silicate weathering, which is achieved by tuning a parameter that represents the contribution of continental basalt

weathering [Berner, 2006b], such that it is at its maximum permissible value. However, the contribution of basalts to continental weathering is also amenable to more direct estimation from geologic data regarding the timing and extent of large igneous provinces and the rate of material subduction driving island arc basalt production.

Motivated by this, here we revisit how tectonic drivers of the long-term carbon cycle have changed over Mesozoic and Cenozoic time. We seek to build an internally consistent forward model, by updating the tectonic forcing factors in our existing "COPSE" biogeochemical model [Bergman *et al.*, 2004] and elaborating the different weathering sinks for CO<sub>2</sub> from granites, basalts, and seafloor alteration—a carbon sequestration process that has been incorporated into models for Precambrian climate [Sleep and Zahnle, 2001; Hayes and Waldbauer, 2006] but has not been assessed fully over the Phanerozoic. We reconstruct terrestrial basaltic area from data on the extent of large igneous provinces and plate subduction rates, and use LIP volume to estimate their contribution to degassing. We also adopt the new reconstruction of degassing by Van Der Meer *et al.* [2014] and revise the uplift forcing in the model (so that it is independent of the strontium isotope record, which the model now seeks to predict). We address whether the resulting model of changes in atmospheric CO<sub>2</sub> is in broad agreement with proxy data for both the Van Der Meer *et al.* [2014] and original GEOCARB degassing scenarios, examine which processes most likely acted to counter the high CO<sub>2</sub> degassing rates reported in the former, and how the contribution of each CO<sub>2</sub> sink has changed over the Mesozoic and Cenozoic.

## 2. Tectonic Controls on the Long-Term Carbon Cycle

The inorganic side of the long-term carbon cycle involves a balance between degassing sources of CO<sub>2</sub> from volcanic and metamorphic processes and weathering sinks of CO<sub>2</sub>, which involve the liberation of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions from silicate rocks and their deposition in carbonate rocks along with oceanic CO<sub>3</sub><sup>2-</sup>. These sources and sinks of CO<sub>2</sub> are affected by changes in tectonic processes, which hence can exert a major control on atmospheric CO<sub>2</sub> concentrations over geologic time.

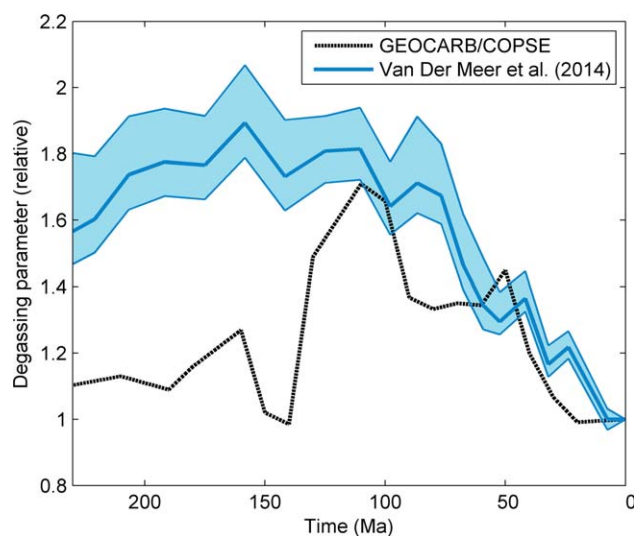
Key long-term sources of CO<sub>2</sub> are metamorphic degassing from carbonates (and organic matter) and direct injection of CO<sub>2</sub> from the mantle. Metamorphic degassing is driven by subduction of oceanic crust at continental margins, and input of mantle CO<sub>2</sub> is associated with crustal production at mid-ocean ridges and with the emplacement of large igneous provinces. LIP emplacement in continental settings also results in contact metamorphism of carbon reservoirs in the adjacent crust [Svensen *et al.*, 2009].

The long-term sinks of CO<sub>2</sub> involve the weathering of subaerial granites and basalts [Dessert *et al.*, 2003], and the carbonatization of seafloor basalts [Gillis and Coogan, 2011]. Uplift of the continents provides a fresh supply of (primarily granitic) material for terrestrial silicate weathering. Subduction-driven arc volcanism and the emplacement of continental LIPs provide basaltic material, which undergoes more rapid silicate weathering. Additionally, seafloor spreading provides a fresh supply of basaltic ocean floor for seafloor carbonatization/alteration, which occurs when warm seawater flows through the crust.

### 2.1. Degassing: Metamorphism, Ridge, and LIPs

We show in Figure 1 a comparison between the recent calculation of global degassing rate based on scaling combined arc and ridge CO<sub>2</sub> degassing to inferred subduction zone length [Van Der Meer *et al.*, 2014] and that previously employed in carbon cycle models, which is based on inversion of paleo-sea level records [Gaffin, 1987] prior to 150 Ma and measurements of trench convergence [Engbretson *et al.*, 1992] since 150 Ma to estimate global spreading rate.

In addition, eruption of large igneous provinces is accompanied by massive CO<sub>2</sub> input over a geologically short time scale (<10<sup>6</sup> years). If input was sufficiently rapid, geochemical box models have predicted very large CO<sub>2</sub> increases (e.g., around a doubling of pre-LIP atmospheric CO<sub>2</sub> concentration for the Siberian traps and Central Atlantic Magmatic Province (CAMP) emplacements, assuming input times between 30 and 500 kyr [Beerling and Berner, 2002; Berner, 2002]). Stabilization of climate occurs in these models after ~2 Myr, but the background forcing scenarios we will consider (i.e., altered degassing rates, weathering regimes, and burial rates) and large weatherable area of some of the LIPs may affect both peak CO<sub>2</sub> concentrations and stabilization times. Shorter term effects such as contact metamorphism of organic sediments and



**Figure 1.** Global CO<sub>2</sub> degassing. Black line shows relative CO<sub>2</sub> degassing rate assumed in previous models GEOCARB [Berner, 2006a] and COPSE [Bergman et al., 2004], among others. Blue shaded area shows recently calculated degassing parameter taking into account subduction zone length [Van Der Meer et al., 2014].

methane release [Svensen et al., 2009] may have led to larger increases in CO<sub>2</sub> and global temperatures following LIP emplacements [Belcher and Mander, 2012].

## 2.2. Silicate Weathering: Granites and Basalts

Dependency of silicate weathering rates on local temperature and runoff allows the carbon burial flux from silicate weathering and carbonate deposition to vary in response to changes in atmospheric CO<sub>2</sub>, resulting in negative feedback which balances the long term carbon cycle [Walker et al., 1981]. As well as changes in temperature, there are many other factors that influence the long term global silicate weathering rate and resulting marine carbonate burial flux.

Enhancements of the weathering flux

may be brought about by increases in global erosion rates [Dixon et al., 2012] (which may lead to changes in climate dependence of weathering [West, 2012]), the presence of land plants (which introduce organic acids as well as physically breaking apart rock) [Berner, 1997], or changes in the hydrological cycle [Maher and Chamberlain, 2014] including the paleolatitude and relative positioning of the continents [Goddéris et al., 2014]. Altering these factors changes the global terrestrial “weatherability”—the total silicate weathering rate under a given CO<sub>2</sub> concentration. A higher weatherability means that the carbon cycle will stabilize with a lower concentration of atmospheric CO<sub>2</sub>, providing the CO<sub>2</sub> degassing rate is unchanged [Kump and Arthur, 1997]. Essentially, the long term stable concentration of CO<sub>2</sub> is determined by a combination of the global degassing rate and the weatherability of terrestrial silicates (and the ocean floor).

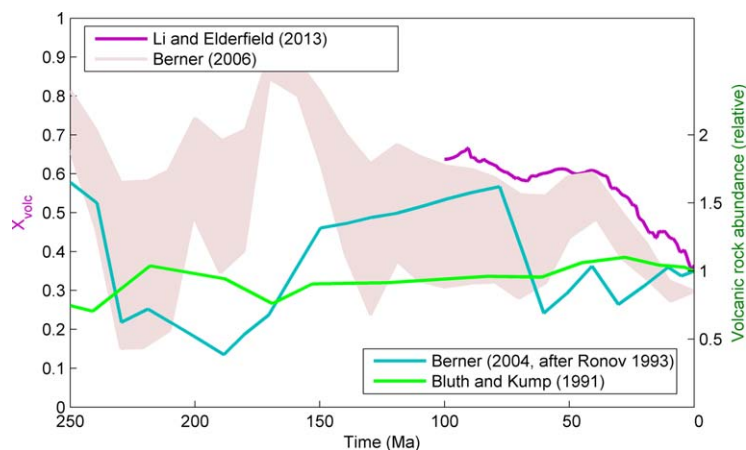
An important factor that influences terrestrial weatherability is the type and area of silicate rock available for weathering. Mafic silicates like basalt weather considerably more rapidly than felsic granites; less than 10% of the global silicate area is basaltic yet this contributes around one third of the silicate weathering flux today [Dessert et al., 2003]. This means that changes in past global basaltic area may have led to significant changes in terrestrial weatherability, and therefore atmospheric CO<sub>2</sub> concentration.

## 2.3. Reconstructing Basalt Weathering

Current reconstructions of volcanic rock weathering (Figure 2) are produced by inversion of the marine <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>187</sup>Os/<sup>188</sup>Os signatures [Berner, 2006b; Li and Elderfield, 2013]. The predominant sources of ocean Sr and Os are the weathering of terrestrial rocks, and there are no fractionation effects associated with weathering and burial of these species. This means that the seawater value, as recorded in sediments, reflects the contribution from different weathering sources and mantle inputs. <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>187</sup>Os/<sup>188</sup>Os of fresh basalt reflects the value of the mantle source rocks, and decay of <sup>87</sup>Rb and <sup>187</sup>Re, respectively, causes the <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>187</sup>Os/<sup>188</sup>Os of older granitic lithologies to be higher than the mantle value.

Berner [2006b] sets <sup>87</sup>Sr/<sup>86</sup>Sr values for bulk volcanic and nonvolcanic silicates to obtain an expression linking the Phanerozoic seawater <sup>87</sup>Sr/<sup>86</sup>Sr curve to the fraction of silicate weathering that was from volcanic sources (denoted  $X_{vol}$ ). Li and Elderfield [2013] model the coupled Sr, Os, and C isotope systems to reconstruct long term carbon cycle fluxes from weathering and burial over the Late Cretaceous and Cenozoic. Both studies suggest a decreasing trend in basalt weathering over most of the Cenozoic. Li and Elderfield [2013] propose that weathering of (island) basalts has decreased in response to an uplift-driven increase in weathering of continental nonbasalt silicates.

However, there are several difficulties in using radiogenic isotope tracers to reconstruct terrestrial weathering regimes. The <sup>87</sup>Sr/<sup>86</sup>Sr of nonvolcanic silicates [Berner, 2006b] and sedimentary carbonates [Boucot and



**Figure 2.** Reconstructions of volcanic weathering.  $X_{volc}$  (left axis) is the fraction of terrestrial silicate weathering that is volcanic (note that this includes contribution from island and arc basalts, which are included under “terrestrial silicates” in our analyses), calculated from inversion of the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{187}\text{Os}/^{188}\text{Os}$  curves [Berner, 2006b; Li and Elderfield, 2013]. Plotted here against relative abundance of volcanic rocks (right axis) [Berner, 2004; Bluth and Kump, 1991; Ronov, 1993].

Gray, 2001] varies greatly due to age and composition of weathered material, ruling out a straightforward link between ocean  $^{87}\text{Sr}/^{86}\text{Sr}$  and fraction of volcanic weathering. Uncertainty in total rates of terrestrial weathering, mantle input and seafloor alteration also make the  $^{87}\text{Sr}/^{86}\text{Sr}$  signal difficult to link directly to the volcanic fraction of weathering. Interpretation of the marine  $^{187}\text{Os}/^{188}\text{Os}$  record is no less straightforward: preferential weathering of ancient shield rocks may result in a very radiogenic signal [Peucker-Ehrenbrink and Blum, 1998], similarly the weathering of more ancient basalts may

impart a significantly more radiogenic signal than their younger counterparts [Gannoun *et al.*, 2006]. Additional Os isotope variation may be associated with spatial heterogeneity in seawater, or by extraterrestrial Os sources such as impact events [Peucker-Ehrenbrink and Ravizza, 2012].

The Sr-derived curves for basalt weathering fraction have a large uncertainty due to the range of possible values for nonvolcanogenic Sr [Berner, 2006b], although predicted values for the Mesozoic are generally higher than the present day, and a decline in volcanic weathering over the Cenozoic is robustly predicted, due to continually rising  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Volcanic weathering reconstructions for the last 100 Myr using constraints from both Sr and Os isotopes [Li and Elderfield, 2013] show a general decline from 100 Ma to present.

Attempts have also been made to reconstruct the relative exposure of volcanics from rock abundance data. Using the historic volcanic rock volumes of Ronov [1993], Berner [2004] normalizes against an exponential loss curve to obtain an estimate of the rate of volcanic eruption over time. This shows above-present-day values for the Cretaceous, but lower-than-present values during the Triassic and Jurassic. However, this interpretation is not directly linked to the exposed area of volcanics to weathering, and the low values reported for ~200 Ma are not easy to reconcile with eruption of the massive Central Atlantic Magmatic Province (CAMP) at this time—which is thought to have emplaced an area of basaltic rock of comparable size to the entire present-day volcanic area [Knight *et al.*, 2004; Marzoli, 1999].

Bluth and Kump [1991] have produced historical land area for different rock units over the Phanerozoic. Assuming that the total area of silicates can be represented by total land area minus the area of carbonates, an expression for the fraction of exposed silicates that are of volcanic origin can be calculated [see Berner, 2006b]. The result is a slight increasing trend from the early Triassic to the present day.

The area of volcanics exposed to weathering during the Mesozoic is therefore very uncertain, with isotope-derived methods generally predicting areas in excess of the present day while rock abundance methods predict values that are lower. Interpretation of rock abundance data is however extremely difficult—normalizing via a single decay curve [Berner, 2004] or by noncarbonate area [Berner, 2006b] necessarily represent generalized preliminary approaches.

#### 2.4. Seafloor Weathering

Low temperature hydrothermal alteration of mid-ocean ridge basalts (or “seafloor weathering”) is a significant long-term carbon sink. If the oceanic crust provides the alkalinity source (via  $\text{Ca}^{2+}$  release), rather than riverine input (as Ca, or via Mg or K followed by cation exchange) [Alt and Teagle, 1999; Coogan and Gillis, 2013], then this operates independently from silicate weathering.



As with continental silicate weathering, it has been proposed that the rate of carbon uptake by the ocean crust is linked to atmospheric CO<sub>2</sub> concentration, resulting in negative feedback on climate. There is no clear direct link [Caldeira, 1995], but two indirect feedback mechanisms have been proposed. In the first, higher atmospheric CO<sub>2</sub> results in increased bottom water temperature, which increases rates of fluid-rock reaction [Brady and Gislason, 1997]. Second, potassium reacts with igneous plagioclase to form K-feldspar and liberate Ca from the oceanic crust (with stoichiometry  $7 \text{ Ca}^{2+} : 2 \text{ K}^+$ , i.e., the oceanic crust providing the majority of the alkalinity [Coogan and Gillis, 2013]). Therefore, increased atmospheric CO<sub>2</sub> should drive increased riverine K input (from continental weathering), ultimately resulting in enhanced seafloor weathering rates [Coogan and Gillis, 2013].

Drill core analysis has confirmed that more carbon is added to the ocean crust under warmer bottom water temperatures [Gillis and Coogan, 2011] and that high K-feldspar abundances are coincident with large fluxes of carbon into the ocean crust [Coogan and Gillis, 2013]. The majority of carbon added to the ocean crust is deposited within 20 Myr of crust formation [Gillis and Coogan, 2011], supporting the assumption that the rate of seafloor weathering is linked to the rate of ocean crust production at mid-ocean ridges through material availability [Sleep and Zahnle, 2001]. However, these feedback relationships are still very uncertain, and the strength of the feedback on CO<sub>2</sub> concentration is unknown. Recent studies investigating seafloor weathering [Hayes and Waldbauer, 2006; Sleep and Zahnle, 2001] assume a simple power law relationship between atmospheric CO<sub>2</sub> and the rate of carbon uptake, based on the laboratory results of Brady and Gislason [1997] for the bottom water temperature feedback. It is possible that the feedback may be substantially stronger or weaker than this.

The rate of seafloor weathering over the Phanerozoic is also unknown. A major complicating factor is that not all of the alkalinity deposited in ocean crust basalts has been weathered from the rock itself, it is possible that over 70% of the calcium may come from seawater [Alt and Teagle, 1999], meaning that much of the CaCO<sub>3</sub> deposited in the crust is linked instead to terrestrial weathering. However, the ocean crust alkalinity budget of Coogan and Gillis [2013] supports a major contribution from seafloor weathering. As indirect support, carbon abundances in the upper ocean crust [Coogan and Gillis, 2013; Gillis and Coogan, 2011] are substantially higher in the late Mesozoic than in the Cenozoic (up to five times higher wt. %), which is consistent with the hypothesis that higher material input from seafloor spreading [Van Der Meer et al., 2014] and atmospheric CO<sub>2</sub> concentrations [Park and Royer, 2011] drove increased seafloor weathering rates.

Berner and Kothavala [2001] add an expression for seafloor weathering to the "GEOCARB 3" model, linking the rate only to seafloor spreading rates, not to CO<sub>2</sub> concentration. Seafloor weathering does not contribute greatly to the carbon cycle in this model as the rate is assumed not to be affected by the high CO<sub>2</sub> concentrations, and the material supply from spreading centres is assumed to be low for much of the Mesozoic, in contrast to recent data [Van Der Meer et al., 2014]. Previous attempts to reproduce the Phanerozoic <sup>87</sup>Sr/<sup>86</sup>Sr curve using a forward model rely on seafloor weathering being a more powerful carbon sink in the past, thus reducing the weathering contribution of the continents [Francois and Walker, 1992].

### 3. Methods

#### 3.1. The COPSE Model

To analyze tectonic effects on climate we use an updated version of the COPSE model [Bergman et al., 2004]. For full model equations see supporting information, for discussion of the original model see the 2004 paper. COPSE is an extension of the GEOCARB [Berner, 1991, 2006a] models that employs a process-based representation of the marine and terrestrial biosphere [Lenton and Watson, 2000] to calculate organic fluxes of carbon and sulphur over Phanerozoic time. The philosophy behind COPSE is to use mechanistic approximations, rather than inversion of isotope records, to calculate geochemical fluxes. This parallels our approach here of reconstructing changes in weathering regimes from primary data rather than "weathering tracers" such as <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>187</sup>Os/<sup>188</sup>Os.

Changes in the global reservoir of atmospheric and ocean carbon (A) are represented by the following differential equation summing CO<sub>2</sub> sources from degassing of carbonates (*ccdeg*), organic material (*ocdeg*), LIP degassing (*LIPdeg*), carbonate weathering (*carbw*), and oxidative weathering of organics (*oxidw*). Sinks are the burial of organic carbon in the marine (*mocb*) and terrestrial (*locb*) environments, carbonate burial (*mccb*), and weathering/alteration of the seafloor (*sfw*)

$$\frac{dA}{dt} = ccdeg^* + ocdeg^* + oxidw + LIPdeg^{**} + carbw - mocb - locb - mccb - sfw^{**} \quad (1)$$

We calculate marine carbonate burial from steady state marine alkalinity balance, assuming the carbonate cycle is at equilibrium, and including the coupling of the oxidative sulphur cycle to alkalinity [Torres et al., 2014]:

$$mccb = silw + carbw - pyr w + mpsb \quad (2)$$

where *mps b* is pyrite sulphur burial, and *pyr w* is pyrite sulphur weathering (in mol S yr<sup>-1</sup>).

Substituting for *mccb* in (1) leads to the net equation:

$$\frac{dA}{dt} = ccdeg^* + ocdeg^* + oxidw + LIPdeg^{**} - mocb - locb - silw^* + (pyr w - mpsb) - sfw^{**}. \quad (3)$$

Here \* refers to fluxes that are updated in this paper while \*\* shows fluxes that have been added to the model for this work.

The addition of sulfide oxidation and sulfate reduction in the carbon cycle [Torres et al., 2014] has little effect in our model, as steady state for the ocean alkalinity is assumed. A more complete ocean model is required to analyze the effects of possible transient CO<sub>2</sub> emissions in a global context.

### 3.2. Modeling CO<sub>2</sub> Input From Metamorphism and Degassing

Our first model runs will consider the metamorphism and ridge contribution of Van Der Meer et al. [2014], which is added to COPSE alongside an explicit representation of LIP CO<sub>2</sub> release. Relative global degassing rate, *D*, acts as a multiplier for the rates of degassing for organic (*ocdeg*) and carbonate carbon (*ccdeg*)

$$ocdeg = k_{ocdeg} \left( \frac{G}{G_0} \right) \times D, \quad (4)$$

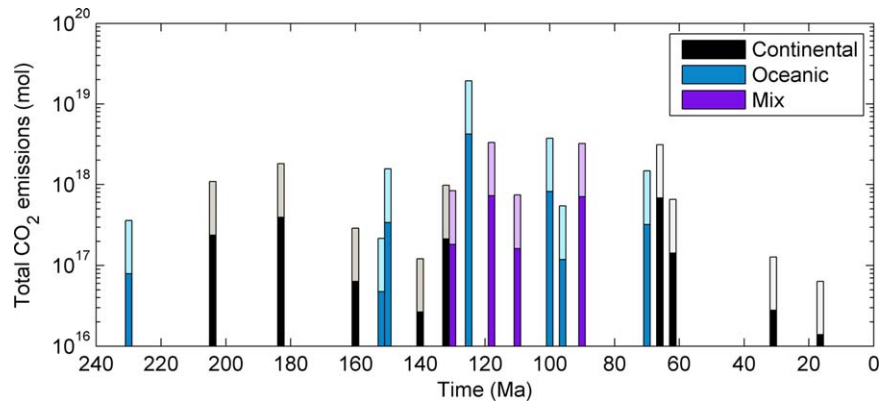
$$ccdeg = k_{ccdeg} \left( \frac{C}{C_0} \right) \times D \times B, \quad (5)$$

where *k<sub>ocdeg</sub>* and *k<sub>ccdeg</sub>* are the present-day rates, *G*, *C* represent the total crustal inventory of organic carbon and carbonate carbon, respectively, and *G<sub>0</sub>*, *C<sub>0</sub>* are their present-day sizes. *B* is the relative carbonate burial depth forcing, which is inherited from COPSE and GEOCARB, and represents the evolution of pelagic calcifiers which increases the amount of carbonate entering subduction zones.

We follow Beerling and Berner [2002] by scaling total LIP CO<sub>2</sub> release to the initial estimated basalt volumes. The timing, initial areas, and tectonic environment (terrestrial versus submarine) of large igneous provinces have been compiled by the Large Igneous Provinces Commission [Ernst and Buchan, 2001; Ernst, 2014] (Figures 3 and 4). We have updated this record where necessary (see supporting information and references therein). Where LIP volumes are unknown, we calculate them by assuming an area-volume relationship based on the more recent and well-preserved LIPs (see supporting information).

Figure 3 shows the volumes and CO<sub>2</sub> release potentials for all LIPs from 230 to 0 Ma. By far the largest volume event over the model timeframe is the ~125 Ma Ontong Java Plateau, with an estimated initial volume of around 5 × 10<sup>7</sup> km<sup>3</sup> [Neal et al., 1997]. This is 10 times the volume of the Siberian traps, which is itself one of the most voluminous LIPs on record. Cumulative CO<sub>2</sub> degassing from LIPs during the last 230 Ma is estimated here as 1–5 × 10<sup>19</sup> moles. This represents around 1% of global cumulative CO<sub>2</sub> degassing over this period, but the geologically short time scale of these degassing events may lead to significant climate impacts.

For a maximum estimate of CO<sub>2</sub> emissions, we assume each LIP degasses over a time scale of 200 kyr [Berner, 2002] and assume the rate of degassing follows a Gaussian curve [Beerling and Berner, 2002]. Although 200 kyr is the “slow degassing” estimate from Berner’s work, more recent compilations suggest LIP degassing time scales are somewhat slower, in the range 500 kyr–3 Myr [Courtillot and Renne, 2003]. We exclude here shorter term effects such as contact metamorphism of organic sediments and methane release [Svensen et al., 2009] as they are difficult to quantify and analyze with our long term model.



**Figure 3.** Submarine and continental LIP emplacement CO<sub>2</sub> emissions. Total moles of carbon degassed as CO<sub>2</sub> during LIP emplacement. Min and max estimates for CO<sub>2</sub> degassing/volume relationship are from *Leavitt [1982]* and *Gerlach and Graeber [1985]*, respectively (following *Beerling and Berner [2002]*) and are denoted by darker and lighter colors, respectively.

### 3.3. Modeling Basalt and Granite Weathering

To obtain estimates for the weathering flux associated with basalts, we include the relative basalt area parameter as a time-dependant forcing in COPSE. The model calculates global silicate weathering rates using the expressions described in the GEOCARB models [*Berner, 1994*], and is modified here by splitting the silicate weathering term into “basalt,” representing volcanics, and “granite,” which represents all non-mafic terrestrial silicates:

$$basw = \%bas_0 \times k_{silw} \times f_{CO2bas} \times PG \times pevol \times BA, \quad (6)$$

$$granw = (1 - \%bas_0) \times k_{silw} \times f_{CO2gran} \times PG \times pevol \times GA \times U, \quad (7)$$

$$silw = basw + granw. \quad (8)$$

Here *basw* and *granw* are the model fluxes for basalt weathering and granite weathering. *U* is normalized uplift rate, which is assumed to affect granites but not basalts, which are presumed to be continually well exposed. *PG* is the runoff modifier due to paleogeographic changes, the constant *%bas<sub>0</sub>* is the present-day fraction of silicate weathering that is basaltic, chosen as 0.35 [*Dessert et al., 2003*] (granite weathering is assumed to make up the remainder of CO<sub>2</sub> consumption via terrestrial silicate weathering), *k<sub>silw</sub>* is the present-day rate of silicate weathering. *BA* is the relative basaltic area (calculated below and shown in Figure 5) and *GA* is the relative area of granites, which is calculated as the total silicate area minus that of continental basalts (see supporting information). *pevol* represents negative feedback on terrestrial weathering due to evolution of land plants, including fire feedback, photorespiration, and CO<sub>2</sub> fertilization as in the original COPSE model. See supporting information and the COPSE paper for full details of the vegetation model. *f<sub>CO2bas</sub>* and *f<sub>CO2gran</sub>* denote the climatic dependency of silicate weathering [*Berner, 1994*], which incorporates plant-CO<sub>2</sub> feedbacks, and the temperature dependencies *f<sub>Tbas</sub>* and *f<sub>Tgran</sub>*, which assume activation energies for basalt and granite weathering of 42 and 50 kJ/mol, respectively [*Dupre et al., 2003*]

$$f_{Tbas} = e^{0.061(T-T_0)} \{1 + 0.038(T-T_0)\}^{0.65}, \quad (9)$$

$$f_{Tgran} = e^{0.072(T-T_0)} \{1 + 0.038(T-T_0)\}^{0.65}. \quad (10)$$

Here *T* is global average surface temperature and *T<sub>0</sub>* is present-day surface temperature.

The uplift/erosion forcing *U* is assumed to influence granite, carbonate and organic carbon (but not basalt) weathering fluxes via supply rate of material. In earlier versions of COPSE, values for *U* over the Phanerozoic are taken from the early GEOCARB models, and were calculated by inverting the strontium isotope record. We follow *Goddéris and Francois [1995]* and *Berner [2006b]* by replacing this with a cubic fit to sediment abundance data [*Ronov, 1993*] in order that no fluxes in the system depend on input of isotope tracer values. We also introduce the expression, *PG*, representing relative changes to global runoff due to changing paleogeography. *PG* is taken from published runs of the GEOCLIMtec model [*Goddéris et al., 2014*] and is assumed to affect all silicate and carbonate weathering fluxes.

Aside from the rock area (BA, GA) forcings, uplift rate, and activation energies, weathering of granites and basalts is assumed to follow the same dependencies. It is probable that factors such as plant cover, paleogeographic position and global runoff affect granite and basalt weathering in different ways. These effects are potentially important, but involve a high degree of uncertainty and require the use of a spatial model to accurately depict them [e.g., Taylor et al., 2012; Lefebvre et al., 2013]. Our modeling implicitly allows for the more rapid weathering of basalts via a simple scaling relationship (i.e., the assumption that doubling the area of exposed basalt will double the weathering flux from basalts).

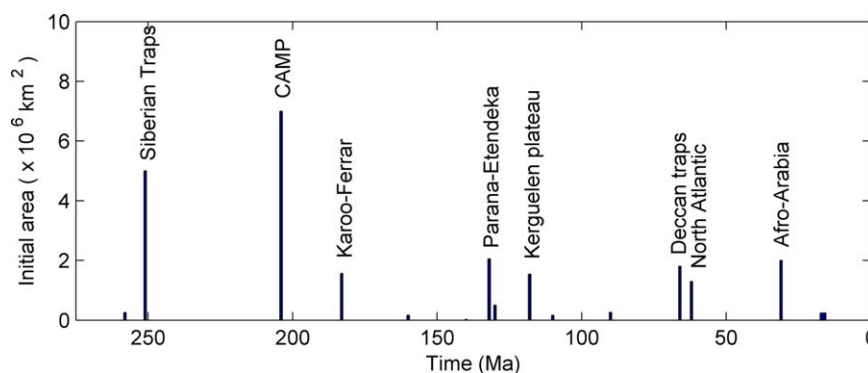
### 3.4. Basaltic Area Reconstruction

We introduce a new method for calculating the past land area covered by basalts, which we reason must be a key driver of the rate of global basalt weathering. The present-day basaltic area is contributed by large igneous provinces, ocean island basalts, and island arcs. The total area has been estimated at  $6.8 \times 10^6 \text{ km}^2$  [Dessert et al., 2003]. Of this,  $2 \times 10^6 \text{ km}^2$  is contributed by ocean island basalt and island arcs [Allègre et al., 2010], with the remaining area related to existing large igneous provinces [Dessert et al., 2003]. In order to reconstruct total terrestrial basaltic area, we adopt an individual approach for each igneous emplacement.

Figure 4 shows the subaerial areas of LIPs emplaced during the Mesozoic and Cenozoic. The named events in the figure are those with areas  $>10^6 \text{ km}^2$ , which contribute almost all of the total emplaced area, and which we term “major events.” To construct the integrated LIP area exposed to subaerial weathering, we assume exponential decay curves for individual LIPs, representing removal by erosion. We set decay constants for each major event so that their present-day area is recovered (see supporting information for a list of these areas). We set a single decay constant that applies to all of the minor events, which is chosen so that present-day total LIP area is  $4.8 \times 10^6 \text{ km}^2$  [Allègre et al., 2010; Dessert et al., 2003]. This constant falls within the range applied to the major LIPs. Submarine LIPs are assumed not to influence terrestrial weathering rates, but do contribute to  $\text{CO}_2$  release and may impact on seafloor weathering. Contributions to seafloor weathering from oceanic LIPs likely occur due to enhanced crustal production during emplacement [i.e., Coffin and Eldholm, 1994], and thus occur on a similar time scale to  $\text{CO}_2$  degassing. We analyze LIP degassing and seafloor weathering enhancements together later in the paper (see Figure 8).

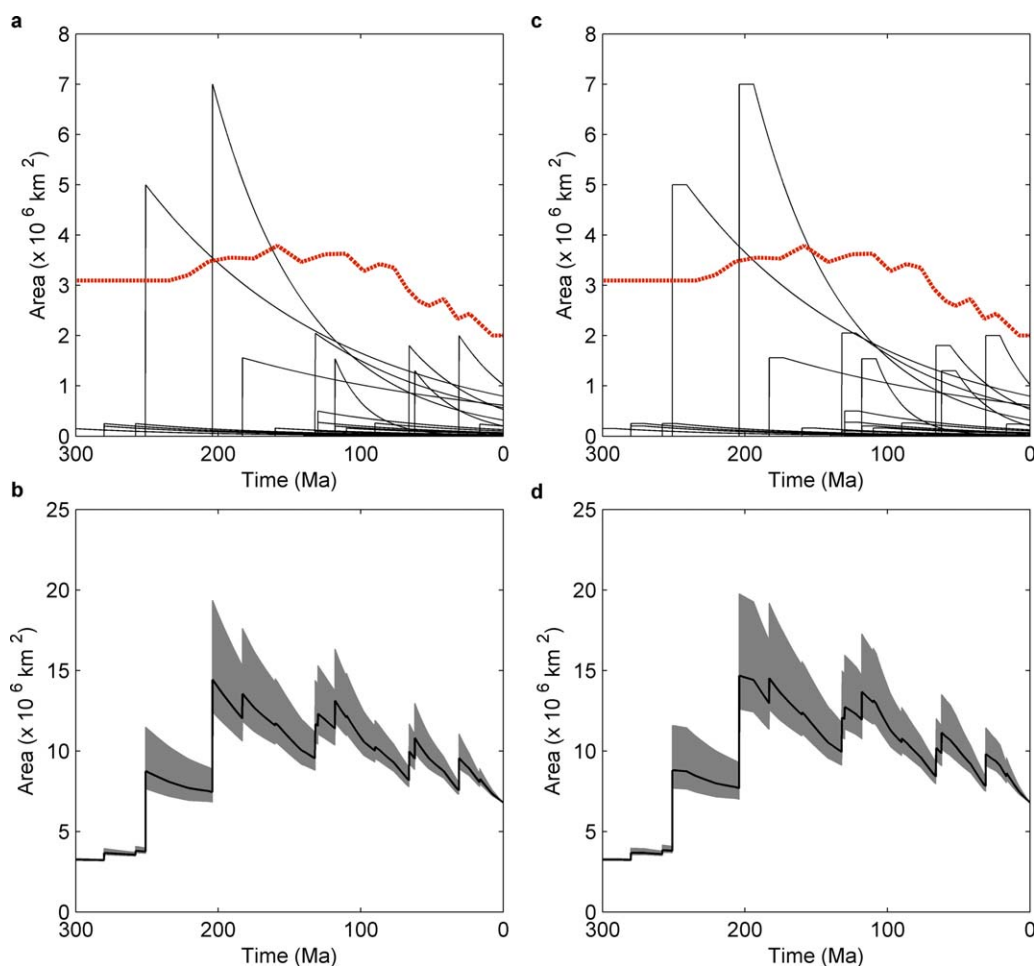
The approach of using exponential decay to account for erosional loss follows Berner [2004], but we apply it here to multiple individual events and to areas rather than volumes. We also trial an alternative approach where decay in area begins 10 Myr after emplacement, representing an assumed 10 Myr volcanic activity where basalt is being emplaced or replenished [Bryan and Ernst, 2008]. Of the present-day island arc and ocean island basalts, 87% of the total area is contributed by island arcs [Allègre et al., 2010], which are driven by crust subduction. We therefore assume that island basalt area (arc and ocean island) scales with the global material subduction rate, which has been estimated for 230 Ma to present [Van Der Meer et al., 2014]. We assume a constant rate before 230 Ma in the absence of data.

The individual LIP decay curves, island basalt area scaling, and resulting global basalt areas are shown in Figure 5. To account for difficulty in initial area estimation and incomplete preservation, we assume an



**Figure 4.** Initial subaerial areas of large igneous provinces. From an updated version of the Large Igneous Provinces Commission A10 database [Ernst and Buchan, 2001; Ernst, 2014] (see supporting information). Note the inclusion of the Kerguelen plateau, which is not a continental flood basalt, but was initially exposed above sea level [Coffin et al., 2000; Mohr et al., 2002].





**Figure 5.** Reconstructed total basalt area for 300 Ma to present. Black decay curves show individual LIP areas, red dashed lines show total island basalt area (ocean islands and island arcs, assumed proportional to ocean crust destruction rate). Gray areas show resulting reconstruction for total basalt area, between 80% and 150% of the initial LIP areas shown in Figure 4 and inclusion of ocean islands and arcs, black lines show the unmodified areas. (a) Exponential decay; (b) resulting total basalt area; (c) delayed exponential decay; (d) resulting basalt area.

uncertainty of  $-20\%$  and  $+50\%$  on initial LIP areas to construct the gray areas in Figures 5b and 5d. This uncertainty window is based on the range of area estimates for well-studied LIPs (e.g., CAMP) [Ernst, 2014; Ernst et al., 2005; Marzoli, 1999], and incorporates the tendency for areas to be revised upward over time. Irrespective of the assumed LIP area and decay curves, the key features of the basalt area reconstruction are a peak after emplacement of the Central Atlantic Magmatic Province around 200 Ma, and a general decline from 200 Ma to present, with a two-stage decline throughout the Cenozoic. The “sawtooth” pattern is a result of the geologically rapid emplacement of LIPs, and the assumed rapid initial decline in area as the weatherable surface is removed. The  $\sim 2$ – $3$ -fold reduction in area between 200 Ma and present is due to the smaller area of more recent LIPs, and a declining rate of material subduction (driving arc basalt production).

The new reconstruction suggests that the global basaltic area was generally larger than the present day during the Jurassic and Cretaceous, due to a series of very large basaltic emplacements that accompanied the breakup phases of Pangaea. Highest values roughly coincide with the start of breakup ( $\sim 175$  Ma) and subsequent smaller peaks are related to the later phases of breakup at  $\sim 140$  and  $\sim 60$  Ma.

A weakness of this approach for calculating basaltic area is the assumption of a constant decay regime over time. It is more likely that decay rates were greatly affected by paleogeographic position and therefore local climate. We believe that this method represents a reasonable first attempt to document integrated basalt area over time from primary data, and expect this type of reconstruction to improve in future work, where

the use of spatial models [Taylor et al., 2012; Lefebvre et al., 2013] can simulate local weathering, erosion, and tectonic regimes—and thus more accurately simulate the removal rates of individual LIPs.

### 3.5. Modeling Seafloor Weathering

The expression for seafloor weathering follows a previous incorporation of this flux into COPSE [Mills et al., 2014], which is based on the model of Sleep and Zahnle [2001]. The CO<sub>2</sub> dependence of seafloor weathering follows Brady and Gislason [1997], assuming that bottom water temperature controls reaction rate. The rate is inferred here from atmospheric CO<sub>2</sub> [Brady and Gislason, 1997] rather than that of the deep water—as has been used by Godd ris and Francois [1995]. Other indirect feedbacks on CO<sub>2</sub> may exist [Coogan and Gillis, 2013] but require quantification.

$$s_{fw} = k_{s_{fw}} \cdot Sp_{rel} \cdot (RCO_2)^\alpha. \quad (11)$$

Here  $Sp_{rel}$  is the relative crustal generation (i.e., spreading) rate,  $RCO_2$  denotes the relative concentration of CO<sub>2</sub> in the atmosphere and  $k_{s_{fw}} = 1.75 \times 10^{12}$  mol/yr is the assumed present-day rate, taken between current estimates [Alt and Teagle, 1999; Gillis and Coogan, 2011; Staudigel et al., 1989].  $\alpha = 0.23$  represents the power of the feedback strength of CO<sub>2</sub> on seafloor weathering [Brady and Gislason, 1997],  $\alpha = 0$  (no feedback on CO<sub>2</sub>) is also trialed. Ocean crust generation rate is assumed to follow the calculated degassing rate of Van Der Meer et al. [2014], following the assumption that plate creation and destruction rates are equivalent over long time scales. We note the limitations of this approximation and that both the present-day rate and the response to CO<sub>2</sub> concentration have large uncertainties attached (see supporting information Figure S1 for the effect of varying present-day rate on the model).

### 3.6. The Strontium Cycle and <sup>87</sup>Sr/<sup>86</sup>Sr

We add to COPSE a strontium isotope system based on the work of Francois and Walker [1992] and Vollstaedt et al. [2014]. Although we do not expect this model to reproduce the ocean <sup>87</sup>Sr/<sup>86</sup>Sr record exactly due to the reservations listed previously, it may be possible to correlate certain features of the record with changes in terrestrial and seafloor weathering regimes. Ocean Sr sources are the weathering of terrestrial granites, basalts and carbonates, and mantle input. The <sup>87</sup>Sr/<sup>86</sup>Sr values of silicates are fixed (with an added expression for increase due to Rb decay), whereas the values for carbonates are allowed to vary depending on buried material. Model Sr sinks are the incorporation of strontium in carbonate sediments and altered seafloor basalt. We stress that an arbitrary error envelope can be added to any model Sr curve due to heterogeneity in terrestrial rock ages, which is not considered here. For full details of the Sr cycle see the SI.

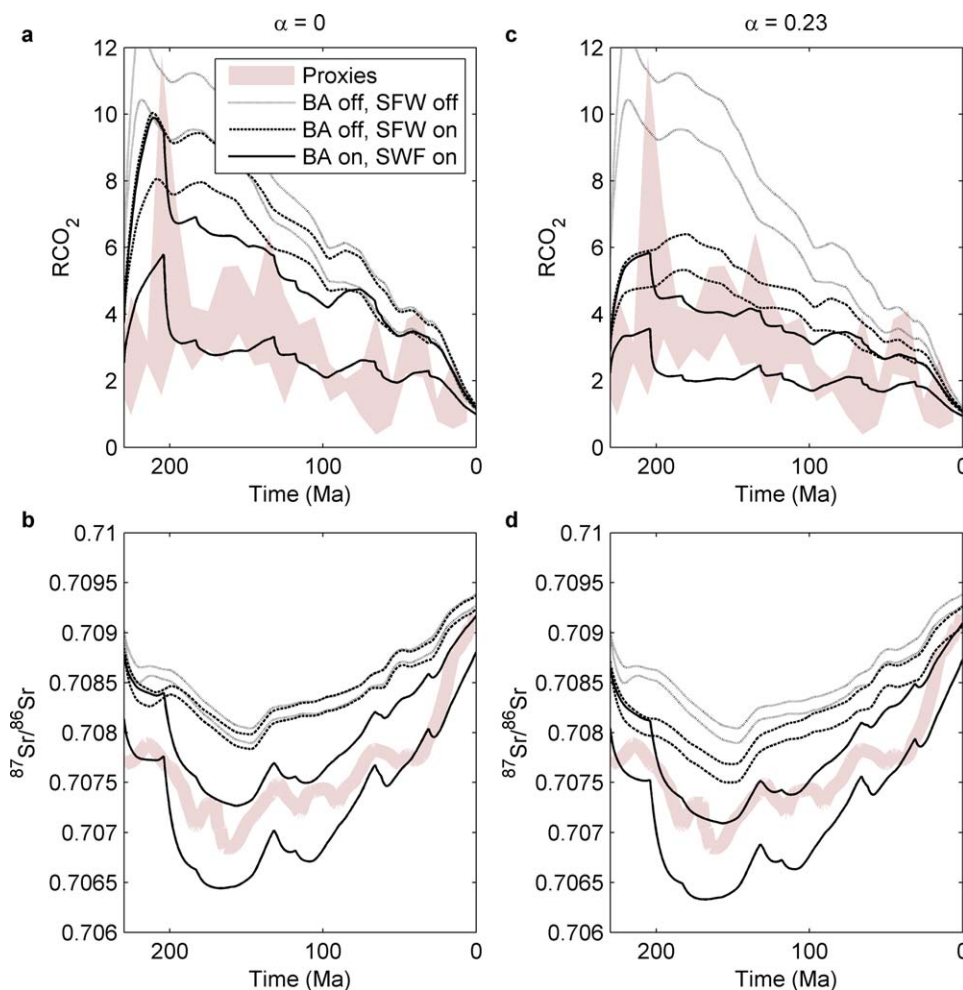
## 4. Model Results and Discussion

### 4.1. Metamorphic Degassing and Weathering

Figure 6 shows COPSE model output for relative atmospheric CO<sub>2</sub> concentration and ocean <sup>87</sup>Sr/<sup>86</sup>Sr for 230–0 Ma when subject to the Van Der Meer et al. [2014] degassing rate. Figures 6a and 6b show results when seafloor weathering is assumed to not be impacted by changing CO<sub>2</sub> concentration ( $\alpha = 0$ ), Figures 6c and 6d show results when the feedback strength is assumed to be that of the bottom water temperature mechanism only ( $\alpha = 0.23$  [Brady and Gislason, 1997]). LIP degassing is not considered here.

Running the default COPSE model (no consideration of basalt or seafloor weathering) with the addition of the recent reconstruction for CO<sub>2</sub> degassing results in high CO<sub>2</sub> concentration for the entire timeframe (dashed gray lines) and shows a poor fit to available proxy data, except for the late Cenozoic [Park and Royer, 2011]. This is because the Van Der Meer et al. [2014] degassing reconstruction is significantly higher than the GEOCARB/COPSE reconstruction over much of the model timeframe.

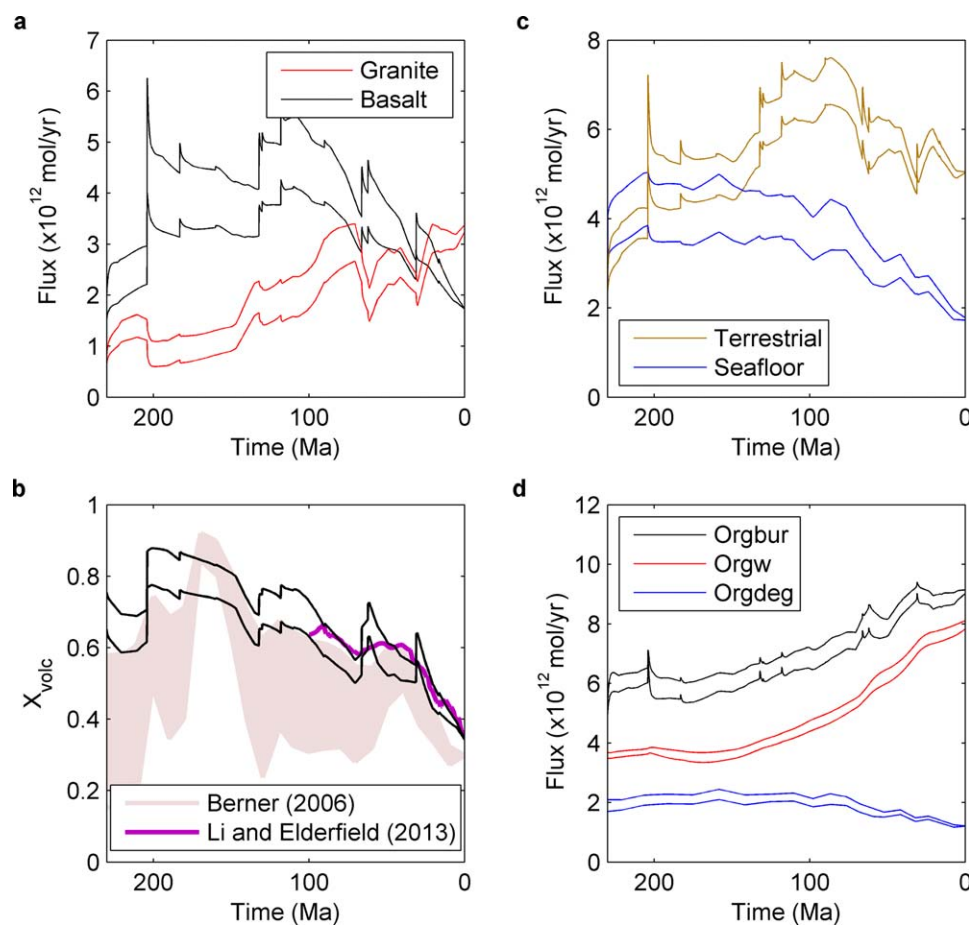
Adding seafloor weathering brings model CO<sub>2</sub> predictions closer to proxy data (black dashed lines). This is because we assume seafloor weathering is enhanced when the mid-ocean production rate is higher, meaning that proposed high degassing rates over the Mesozoic may have been countered by an increase in carbon sequestration via seafloor weathering. Allowing seafloor weathering to also respond to changes in CO<sub>2</sub> ( $\alpha = 0.23$ ; Figures 6c and 6d) results in stronger regulation and lower predicted CO<sub>2</sub> concentrations. Under the addition of basalt and seafloor weathering, predicted CO<sub>2</sub> concentration is further reduced and now reasonably in line with geologic estimates for  $\alpha = 0.23$ . The larger basalt area in the Mesozoic acts to increase global terrestrial weatherability, which leads to lower steady state CO<sub>2</sub> concentration.



**Figure 6.** COPSE model output for 230–0 Ma when subject to basalt weathering and seafloor weathering. (a, c) Relative CO<sub>2</sub> concentration. (b, d) Predicted ocean <sup>87</sup>Sr/<sup>86</sup>Sr. Gray dashed lines show COPSE model with updated degassing forcing [Van Der Meer *et al.*, 2014] but without inclusion of basalt and seafloor weathering. Black dashed lines show inclusion of seafloor weathering only. The two lines represent the upper and lower bounds of the degassing data in Van Der Meer *et al.* [2014]. Black lines show model solution space under inclusion of seafloor weathering and combined basalt areas from Figure 5. Pink areas show data for CO<sub>2</sub> [Park and Royer, 2011] and ocean <sup>87</sup>Sr/<sup>86</sup>Sr [McArthur *et al.*, 2001].

The choice of LIP decay curves and uncertainty on initial LIP areas does not cause large variation in CO<sub>2</sub> predictions—the majority of the variation comes from the uncertainty in the degassing rate. This is expected as these modifications do not lead to large changes in the overall basalt area forcing (Figure 5). When LIP area is increased, CO<sub>2</sub> predictions are lower, as would be expected under increased terrestrial weatherability. The largest changes to CO<sub>2</sub> predictions between the different model setups are during the Jurassic and Cretaceous, where there is assumed to be a large weatherable volcanic area, and a high global spreading rate. Decline in basaltic area over the Cenozoic causes a reduction in terrestrial weatherability, which along with the decreasing seafloor spreading rate, brings predictions closer to the unforced model. CO<sub>2</sub> predictions for 100–75 Ma do not fit well with proxy data for any scenario, indicating either an error in one of the model forcings or mechanisms, or perhaps in the proxy data.

It appears that to counter high degassing rates during the Mesozoic may require some feedback between seafloor weathering rate and CO<sub>2</sub> concentration. Assuming no relationship between seafloor weathering and CO<sub>2</sub>, we must assume very large areas for LIPs and minimum estimates for degassing in order to match proxy data (Figure 6a). In the modification of GEOCARB by Van Der Meer *et al.* [2014], low CO<sub>2</sub> is achieved under the high Mesozoic degassing rate without the addition of seafloor weathering. This requires the



**Figure 7.** Weathering fluxes over model timeframe for  $\alpha = 0.23$ . (a) Terrestrial weathering of basalts (black) versus granites (red, assumed to make up the rest of terrestrial silicates). (b) Fraction of carbon flux from terrestrial silicate weathering that is the result of basalt weathering, compared to the same variable derived from isotope inversion models [Berner, 2006b; Li and Elderfield, 2013]. (c) Terrestrial silicate weathering (brown) versus seafloor weathering (blue). (d) Organic carbon fluxes for burial (black), weathering (red) and degassing (blue).

maximum basalt weathering forcing from GEOCARB (their scenario with  $NV = 0$  corresponds to the very top of the  $X_{volc}$  distribution of Berner [2006b]).

The unforced COPSE model (gray dashed line, Figure 6) shows a very poor fit to ocean  $^{87}\text{Sr}/^{86}\text{Sr}$  data, which is to be expected as the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of terrestrial rock is fixed at the average crustal value. The trend in this output therefore reflects the total terrestrial silicate weathering flux, and the gradually increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  values due to  $^{87}\text{Rb}$  decay. Adding seafloor weathering improves the fit very slightly by removing some of the terrestrial source of radiogenic Sr, which has been shown previously [Francois and Walker, 1992]. Adding seafloor weathering and basalt weathering to the model results in improved prediction of the  $^{87}\text{Sr}/^{86}\text{Sr}$  record; increased weathering of low- $^{87}\text{Sr}/^{86}\text{Sr}$  basalts over the Mesozoic lowers the curve significantly, and peaks followed by declining trends at  $\sim 200$  Ma,  $\sim 130$  Ma and  $\sim 65$  Ma are reproduced to some extent—due to peaks in the basalt area forcing which result from emplacement of large igneous provinces at these times. The peaks in the Sr prediction correspond to decreasing basalt area before LIP emplacement events, poor replication of  $^{87}\text{Sr}/^{86}\text{Sr}$  prior to 200 Ma may be related to the increased uncertainty on the areas of older LIPs.

As with any Sr isotope model, the results depend greatly on the assumed values for  $^{87}\text{Sr}/^{86}\text{Sr}$  of carbonates. For all model runs we assume a starting value for carbonate  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.714, which allows recovery of present-day ocean  $^{87}\text{Sr}/^{86}\text{Sr}$  in the baseline model.  $^{87}\text{Sr}/^{86}\text{Sr}$  of carbonates is a dynamic variable in the model, and reflects changes in the source and sink fractionations. Thus, over the model timeframe the  $^{87}\text{Sr}/^{86}\text{Sr}$  of carbonates decreases due to burial of unradiogenic material to  $\sim 0.7075$  at the present day, which is close to current values for carbonate weathering (0.7077) [Li et al., 2009]. However, our reasonably

successful reproduction of ocean  $^{87}\text{Sr}/^{86}\text{Sr}$  represents only one way of achieving this. Assuming different starting values and changes in carbonate  $^{87}\text{Sr}/^{86}\text{Sr}$  (i.e., due to heterogeneous weathering of rocks of differing ages) could lead to accurate prediction of ocean  $^{87}\text{Sr}/^{86}\text{Sr}$  under different tectonic and weathering regimes.

Our method does however show that the weathering regimes predicted by the model are not falsified by strontium data, and we believe it also provides an encouraging hypothesis for changes in Mesozoic-Cenozoic  $^{87}\text{Sr}/^{86}\text{Sr}$ . *Van Der Meer et al.* [2014] have shown that the general long-term trend in the  $^{87}\text{Sr}/^{86}\text{Sr}$  curve may be related to weathering of volcanic rocks and mantle inputs associated with their degassing reconstruction, we add to this that the finer-scale details may be attributed to the emplacement of large igneous provinces. Even so, our model fails to completely capture the rapidity of the  $^{87}\text{Sr}/^{86}\text{Sr}$  rise over the last 40 Myrs. This may be attributed to extremely radiogenic Sr sources from Himalayan rivers [*Galy et al.*, 1999], which exceed our assumed  $^{87}\text{Sr}/^{86}\text{Sr}$  of “granitic” rocks, or to a more rapid uplift effect than is used in the model. However, model integrations under the more rapid Cenozoic uplift reconstruction of *Hay et al.* [2006] do not show an improved fit to strontium or  $\text{CO}_2$  data (see supporting information Figure S2).

Figure 7 shows the shifts between basalt, granite, and seafloor weathering regimes as predicted by the forward model. Results imply that basalt was the greater contributor to total terrestrial silicate weathering during the Triassic, Jurassic, and Cretaceous. During the Cenozoic, basalt weathering decreases significantly while granite weathering increases somewhat, becoming the greater flux in the last  $\sim 20$  Myr. Total terrestrial silicate weathering peaks around 100 Ma, driven by a very large basalt weathering flux at this time.

Comparing the model output for the volcanic fraction (i.e., basalt fraction) of terrestrial silicate weathering ( $X_{\text{volc}}$ ; Figure 7b) to the same parameter calculated from isotope inverse modeling by *Berner* [2006b] shows that we are at the upper end of Berner’s estimates over the model timeframe. A key point of agreement is the middle to late Jurassic ( $\sim 175$ – $150$  Ma), where Berner’s isotope inversion requires around 80–90% of silicate weathering to come from basalts in order to match the extremely low  $^{87}\text{Sr}/^{86}\text{Sr}$  values for this time. Our model replicates the minimum in  $^{87}\text{Sr}/^{86}\text{Sr}$  at this time under  $X_{\text{volc}} \approx 0.8$ . Our predictions of  $X_{\text{volc}}$  agree well over the past 100 Myr with the inverse model inferences of *Li and Elderfield* [2013].

This work, Berner’s isotope inversion, and the multiple-isotope-inversion model of *Li and Elderfield* [2013] all predict a reduction in the volcanic fraction of terrestrial silicate weathering over the Cenozoic. Our model can assign a definite cause for this—the decrease in basalt area due to falling rate of high-area LIP emplacement and falling subduction rates (driving arc volcanism). The decrease in Cenozoic  $X_{\text{volc}}$  in our model is comparable to these other approaches, consistent with a reasonable reproduction of the rise in  $^{87}\text{Sr}/^{86}\text{Sr}$ .

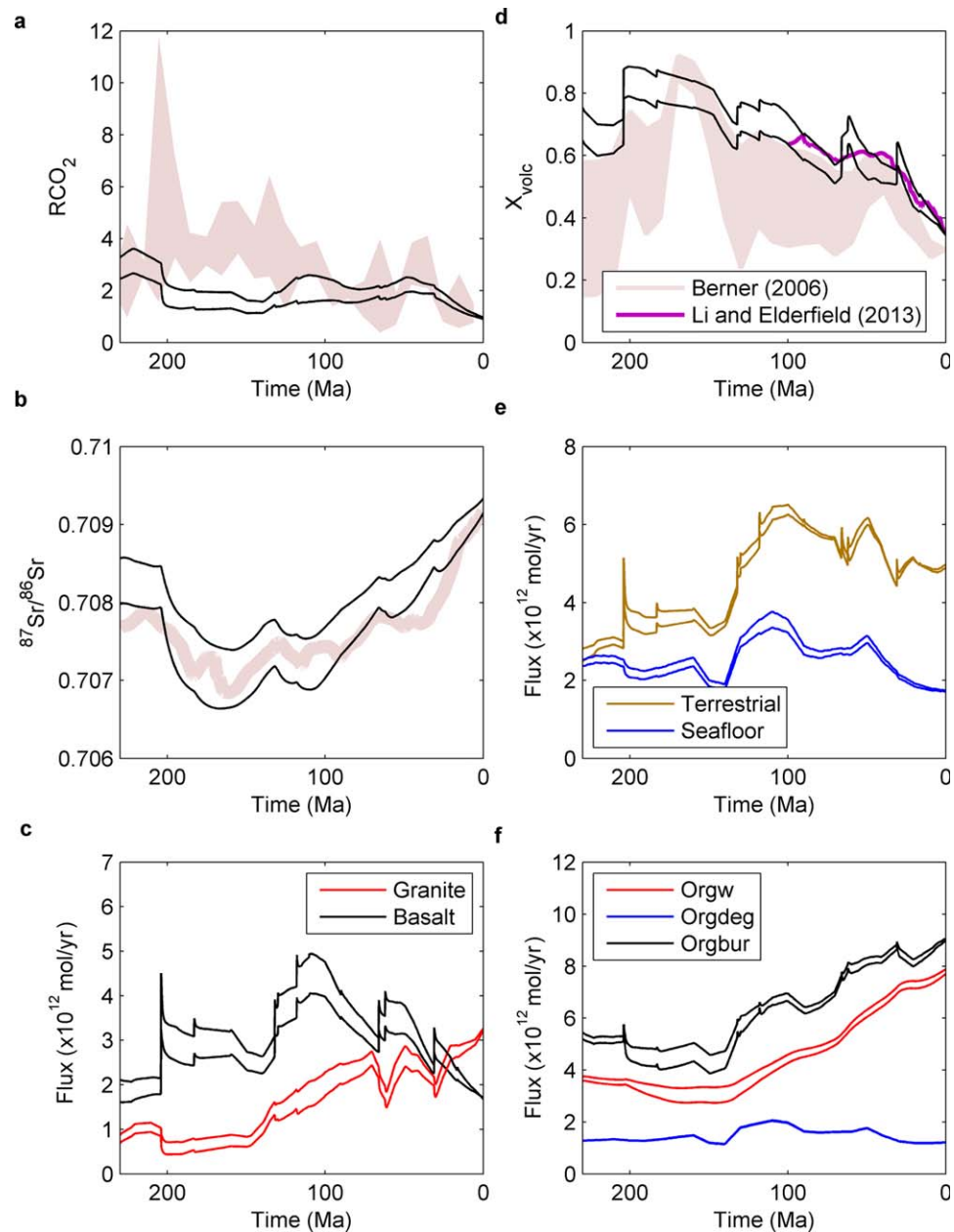
Figure 7c compares weathering fluxes from total terrestrial silicates (all basalt + granite) with seafloor weathering. The two fluxes generally follow the same pattern, which is expected as they both are dependent on atmospheric  $\text{CO}_2$  concentration. However, the fluxes begin to diverge around 150 Ma, meaning that for 230–150 Ma seafloor weathering is similarly important as terrestrial silicate weathering in the carbon cycle, and for 150–0 Ma the terrestrial flux gradually becomes much more important. This shift is due to enhancement of terrestrial weathering fluxes in COPSE-driven by increasing uplift rates and the evolution of angiosperms on the land surface, and also driven by decreasing rates of ocean ridge production—which weaken the seafloor weathering sink. These factors combine to shift the balance of  $\text{CO}_2$  sinks away from seafloor alteration and toward terrestrial silicate weathering [*Mills et al.*, 2014].

This supports the hypothesis, based on a fivefold decrease in calcite concentrations in the upper oceanic crust, that seafloor weathering was a stronger climate regulator during the Mesozoic, and had a less important role in the Cenozoic [*Coogan and Gillis*, 2013], although determining the source of calcite in seafloor basalts still poses a problem. It also makes the suggestion that this switch was driven by a combination of tectonic and biotic processes.

Figure 7d shows the model organic carbon fluxes, which are largely controlled by erosion rates, and thus follow the uplift forcing, aside from organic carbon degassing at subduction zones, which scales with the degassing forcing. Rapid emplacement of LIPs is predicted to drive spikes in organic carbon burial due to additional nutrient delivery from fresh basaltic terrains.

In Figure 8, we revisit the degassing scenario used in the original GEOCARB and COPSE models (see Figure 1). The degassing curve is similar to the estimations of *Van Der Meer et al.* [2014] for 100–0 Ma but the GEOCARB approximation has much lower values, close to the present day, for 230–100 Ma. As would be





**Figure 8.** COPSE model output for 230–0 Ma when subject to basalt weathering and seafloor weathering ( $\alpha = 0.23$ ), under original GEOCARB degassing scenario (see Figure 1). (a) Relative CO<sub>2</sub> concentration. (b) Predicted ocean <sup>87</sup>Sr/<sup>86</sup>Sr. (c) Weathering of basalts (black) and granites (red). (d) Fraction of carbon flux from terrestrial silicate weathering that is the result of basalt weathering, compared to the same variable derived from isotope inversion models [Berner, 2006b; Li and Elderfield, 2013]. (e) Terrestrial silicate weathering (brown) versus seafloor weathering (blue). (f) Organic carbon fluxes for burial (black), weathering (red) and degassing (blue). Areas show model solution space under inclusion of CO<sub>2</sub> degassing scenarios, seafloor weathering and total basalt areas from Figure 5. Pink areas show data for CO<sub>2</sub> [Park and Royer, 2011] and ocean <sup>87</sup>Sr/<sup>86</sup>Sr [McArthur et al., 2001].

expected, modeled CO<sub>2</sub> concentrations for 230–100 Ma are now considerably lower than proxy estimates. Under GEOCARB degassing, seafloor weathering remains smaller than terrestrial silicate weathering for the whole model timeframe, and does not show significant step change between the Mesozoic and present day. Granite and basalt weathering fluxes are also lowered for 230–100 Ma, as is required to balance the carbon cycle, but the volcanic fraction of weathering ( $X_{volc}$ ) remains similar.

Our modeling lends support to the degassing reconstruction of Van Der Meer et al. [2014], reasoning that the large area of weatherable basalts expected during the early and mid-Mesozoic would imply much lower

CO<sub>2</sub> than suggested by proxies [Park and Royer, 2011], unless countered by higher degassing rates. Low Mesozoic degassing would have to be accompanied by much smaller basalt and seafloor weathering fluxes in order to reproduce CO<sub>2</sub> proxies, which has been assumed in previous models, but we question here.

Although our modeling can reproduce CO<sub>2</sub> proxies reasonably, many features of the proxy record are not reproduced, such as high early Cenozoic CO<sub>2</sub>. It may be that using spatial paleogeographic reconstructions will allow models to match these data, or there may be further important mechanisms that are missing from current models.

#### 4.2. CO<sub>2</sub> Input and Seafloor Weathering Due to LIP Emplacement

Figure 9 shows model predictions for CO<sub>2</sub> and <sup>87</sup>Sr/<sup>86</sup>Sr when subject to LIP CO<sub>2</sub> degassing alongside the forcing factors in Figure 6 ( $\alpha = 0.23$  case). This scenario assumes the Van Der Meer *et al.* [2014] global degassing curve and that each LIP degasses over 200 kyr. The result is a series of spikes in CO<sub>2</sub> concentration, which cause small positive “humps” in <sup>87</sup>Sr/<sup>86</sup>Sr due to increased terrestrial weathering as a result of rising temperature. Assuming the minimum amount of CO<sub>2</sub> per km<sup>3</sup> of basalt, the degassing does not significantly alter model predictions. Taking a maximum assumption here results in clear CO<sub>2</sub> spikes, with the atmosphere and ocean CO<sub>2</sub> inventory almost doubling during eruption of the Ontong-Java plateau. Other LIPs result in fairly modest long-term CO<sub>2</sub> rises, even when taking a maximum estimate for the CO<sub>2</sub>-volume relationship.

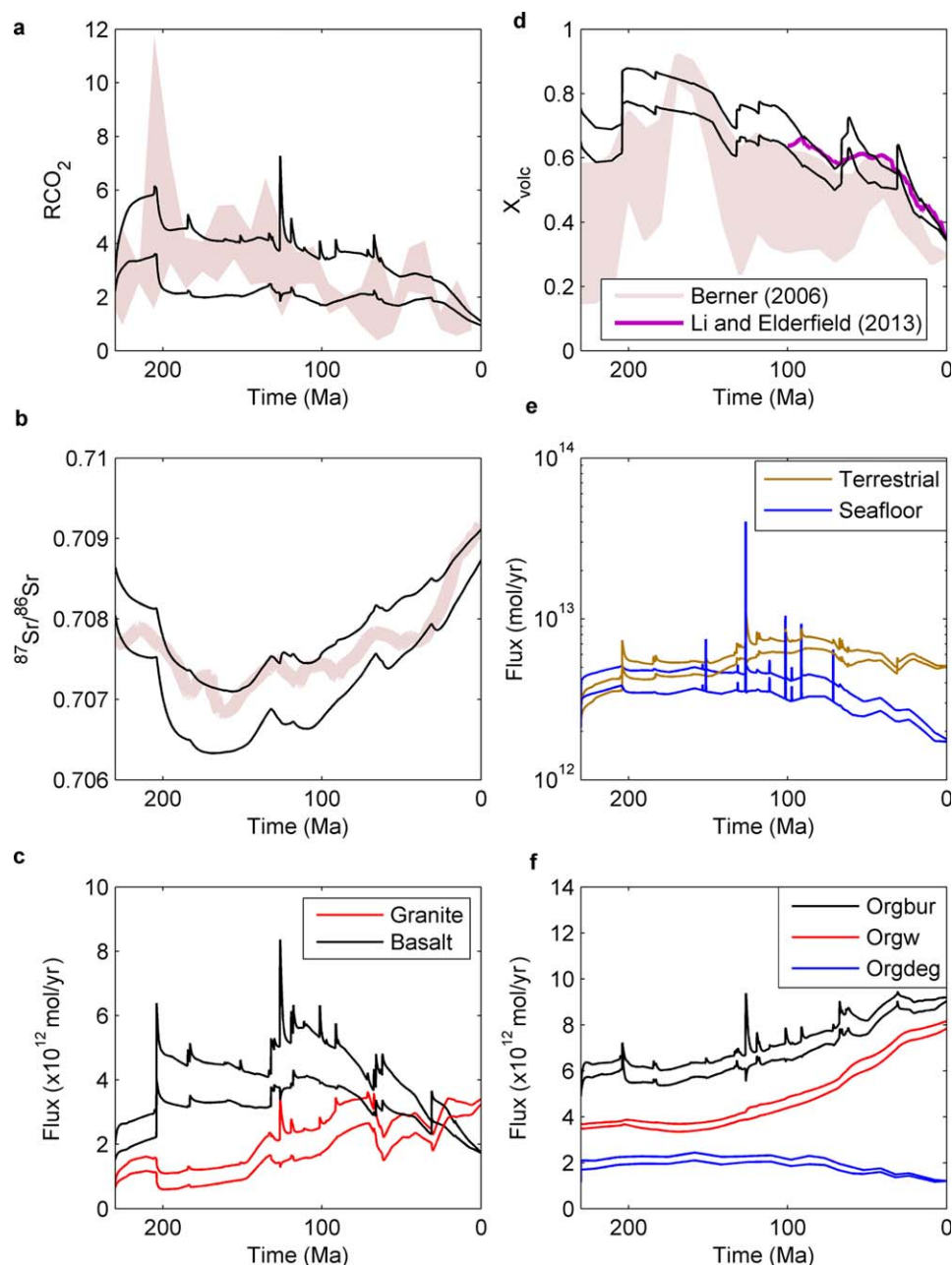
The CAMP emplacement results in only a minor increase in atmospheric CO<sub>2</sub> concentration in our model, in contrast to the ~50% increase shown in the similar carbon cycle model of Beerling and Berner [2002] (the model run in question assumes ~13,000GtC emissions, roughly equal to our maximum of 10<sup>18</sup> mol C). The difference can be accounted for by our consideration of the weathering of CAMP basalts, which partially nullify the CO<sub>2</sub> rise by increasing global weatherability, eventually bringing CO<sub>2</sub> to a steady state lower than the pre-CAMP value. Additionally, COPSE includes negative feedback on CO<sub>2</sub> via a nutrient-driven biosphere, which responds to enhanced weathering by burying more organic carbon (Figure 9f). Our assumption of higher background degassing (and therefore weathering) rates for the Mesozoic also reduces the effectiveness of adding more CO<sub>2</sub> (i.e., the fractional increase in CO<sub>2</sub> input is less). We therefore propose that unless injection is geologically very rapid (<10<sup>5</sup> years), the long term effects of CO<sub>2</sub> emissions from continental flood basalts may be substantially reduced by the associated highly weatherable rock areas that are emplaced. This work however does not consider potential climate drivers from mass extinctions and short term carbonate system feedbacks, which may have a substantial effect over shorter time scales. We also do not consider the changing proportion of ocean/atmosphere carbon that is contained in the atmosphere, which may be boosted by rapid injection before equilibrium is reached.

Submarine LIPs are assumed to influence seafloor weathering rates via increasing crustal production rates, which leads to damping of the associated CO<sub>2</sub> spikes. In the 200 kyr degassing scenarios shown, seafloor weathering rates are increased dramatically during the emplacement of Cretaceous ocean plateaux, and by an order of magnitude during the Ontong-Java emplacement (125 Ma). Assuming the minimum CO<sub>2</sub> degassing for the Ontong-Java leads to brief CO<sub>2</sub> decrease in the model, as enhancement of seafloor weathering outweighs the CO<sub>2</sub> source. Our approach here is preliminary, but may help to reconcile apparent falling Cretaceous CO<sub>2</sub> concentrations with such large CO<sub>2</sub> injection events. It should be noted that short term CO<sub>2</sub> variations resulting from oceanic LIP emplacements require much more detailed study, and an improved understanding of hydrothermal circulation within and around ocean plateaux to properly quantify their contribution to seafloor weathering.

Degassing times for LIPs may be significantly longer than 200 kyrs. Model runs under longer (typically 0.5–3 Myr) emplacement times, as compiled by Courtillot and Renne [2003], show a reduction in the magnitude of CO<sub>2</sub> spikes, and seafloor weathering enhancements (supporting information Figure S3). Although the Ontong-Java plateau still causes a significant perturbation.

## 5. Summary and Conclusions

Our forward model reproduces Mesozoic and Cenozoic CO<sub>2</sub> concentrations satisfactorily, and correctly predicts many of the aspects of ocean <sup>87</sup>Sr/<sup>86</sup>Sr. It appears that recently-inferred high degassing rates during the Mesozoic [Van Der Meer *et al.*, 2014], if correct, would have been countered by increased rates of both



**Figure 9.** COPSE model output for 230–0 Ma when subject to basalt weathering and seafloor weathering ( $\alpha = 0.23$ ), with LIP CO<sub>2</sub> releases over 200 kyr, and seafloor weathering rate dependent on LIP crustal generation. (a) Relative CO<sub>2</sub> concentration. (b) Predicted ocean <sup>87</sup>Sr/<sup>86</sup>Sr. (c) Weathering of basalts (black) and granites (red). (d) Fraction of carbon flux from terrestrial silicate weathering that is the result of basalt weathering, compared to the same variable derived from isotope inversion models [Berner, 2006b; Li and Elderfield, 2013]. (e) Terrestrial silicate weathering (brown) versus seafloor weathering (blue). (f) Organic carbon fluxes for burial (black), weathering (red) and degassing (blue). Areas show model solution space under inclusion of CO<sub>2</sub> degassing scenarios, seafloor weathering and all terrestrial basalt areas from Figure 5. Pink areas show data for CO<sub>2</sub> [Park and Royer, 2011] and ocean <sup>87</sup>Sr/<sup>86</sup>Sr [McArthur et al., 2001].

seafloor weathering and basalt weathering over this era, and not by basalt weathering alone. Consideration of the paleolatitude of LIPs and local hydrological regimes in future models could result in <sup>87</sup>Sr/<sup>86</sup>Sr predictions falling even closer to the geologic record. While our model does include an increase in uplift during the Cenozoic [Raymo and Ruddiman, 1992], this is not the dominant factor driving Cenozoic CO<sub>2</sub> drawdown or the modeled rise in <sup>87</sup>Sr/<sup>86</sup>Sr. Instead, the drop in CO<sub>2</sub> is dominated by declining degassing (see supporting information Figure S4 for a model run with constant degassing) and the rise in <sup>87</sup>Sr/<sup>86</sup>Sr is dominated by decreasing area of basalts undergoing weathering (Figure 6).

Our model defines three climate modes: Pre-Cretaceous CO<sub>2</sub> regulation is split almost equally between seafloor and terrestrial weathering, with basalt weathering exceeding granite weathering. During the Cretaceous, regulation begins to rely more heavily on terrestrial weathering, with basalt weathering still exceeding granite weathering, and Cenozoic regulation is still primarily terrestrial, but sees granites taking over from basalts. This distinction between weathering sources may be very important for the delivery of the limiting nutrient phosphate, and resulting oxygenation through organic carbon burial. Seafloor weathering does not result in P input [Mills *et al.*, 2014] and phosphate availability differs between granites and basalts [Porder and Ramachandran, 2013]. Our results are dependent on the assumed CO<sub>2</sub> degassing curve: predictions for Mesozoic CO<sub>2</sub> concentration appear to support high degassing during this time [Van Der Meer *et al.*, 2014]; however, the notion of a definitive reconstruction of degassing rates is far from resolved.

We have reconstructed the global basaltic area from primary data and simple decay relationships. Modeled basalt weathering under this constraint agrees well with the trends derived from isotope inversion methods [Berner, 2006b; Li and Elderfield, 2013]. The shift from basalt to nonbasalt weathering during the Cenozoic has been attributed to Himalayan uplift enhancing the nonbasalt flux [Li and Elderfield, 2013]. Here we conclude that a ~50% reduction in basaltic area during the Cenozoic was a key factor in reducing the silicate weathering flux from basalts over this time. The increased proportional weathering of granites over the Cenozoic in our model is a response to decreased basalt weathering, as well as uplift of granites—thus the “seesaw” carbon cycle of the Cenozoic [Li and Elderfield, 2013] may be controlled by either basalt or granite weathering enhancements.

Including additional isotope systems will enable these scenarios to be further tested. The Cenozoic lithium isotope record [Misra and Froelich, 2012] shows a rise in  $\delta^7\text{Li}$  of ~9‰. This suggests [Misra and Froelich, 2012; Froelich and Misra, 2014] a change in terrestrial weathering regime from a supply limited Paleocene to a less-intense, kinetically limited present day, combined with a shift in seafloor sinks with an increase in removal by reverse-weathering (removal into sedimentary clays) relative to altered basalt [Li and West, 2014]. This is broadly consistent with our model results (with a decrease in temperature and increase in erosion over the Cenozoic). The model here also suggests additional factors that may contribute: the shift from basalt (with lower incongruent weathering [Misra and Froelich, 2012]) to granite weathering, and a decline in degassing (reducing both terrestrial silicate weathering intensity and low-temperature seafloor basalt alteration).

Long term CO<sub>2</sub> release from continental LIPs is countered in our model by the weathering effects of the newly emplaced basaltic area, as has been established by individual studies of these events [Dessert *et al.*, 2001; Grard *et al.*, 2005]. Large increases in CO<sub>2</sub> concentration associated with LIPs require geologically rapid CO<sub>2</sub> injection, or rely on shorter-term processes such as emissions from intrusion into organic materials and destabilization of methane hydrates [e.g., Beerling and Berner, 2002]. Similarly, CO<sub>2</sub> input from oceanic LIPs may be countered by increased seafloor basalt alteration.

The breakup phases of Pangaea are times of enhanced CO<sub>2</sub> degassing, but also seem to correlate with high proportions of weatherable volcanic area and enhancements of seafloor weathering. This seems plausible given that both LIP emplacements and continental breakup may be driven to some extent by mantle plumes and enhanced crustal production.

Recent spatial simulations of LIP locations for several time points during the Cenozoic [Lefebvre *et al.*, 2013] suggest that weathering of igneous provinces may have generally increased over this time as LIPs encounter different regional climates. This trend appears contrary to the results shown here (see supporting information Figure S4 for a comparison), and does not show the decrease which we attribute to decay of LIP areas. Future work must focus on incorporating both local climatic changes [Lefebvre *et al.*, 2013; Kent and Muttoni, 2013] and reconstructions of previous basalt areas into a dynamic model, in order to more accurately represent changing tectonic drivers of climate.

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