The importance of terrestrial rock weathering as a negative feedback mechanism on the global carbon cycle and climate: a modeling perspective

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ABSTRACT

This thesis presents a set of model studies of climate interactions with terrestrial rock weathering using the University of Victoria Earth System Climate Model (UVic ESCM); several different sets of weathering parameterizations are investigated within the context of two very important periods of Earth's climatic history. Firstly, we examine the importance of the rock weathering feedback mechanism during the last deglacial period (ca. 16,000 - 4,000 BCE) with four box-model parameterizations of terrestrial weathering. The deglacial climate change in the model was driven by changes in orbital parameters, prescribed atmospheric CO₂ variability, and prescribed removal of continental ice sheets. Over the course of the 12,000-year simulation period, increases in weathering provided a mechanism that slowly removes CO₂ from the atmosphere, in opposition to the observed atmospheric CO_2 increase during this period. These processes were found to transfer both carbon and alkalinity to the ocean, the combination of which resulted in as much as a 1000 Pg C increase in total ocean carbon, relative to a control simulation with constant weathering. However, the rapid expansion of northern Hemisphere vegetation introduced a significant uncertainty among the weathering parameterizations. Further experiments to test the individual impacts of weathering dissolved inorganic carbon and alkalinity fluxes on ocean biogeochemistry suggested that the worldwide distribution of rock types and the ratio of carbonate to silicate weathering may be crucially important in obtaining an accurate estimate of changes in global weathering rates.

Secondly, we describe the development and application of a new spatially-explicit weathering scheme. We integrated a dataset of modern-day lithology with a number of previously devised parameterizations for weathering dependency on temperature, primary productivity, and runoff. We tested the model with simulations of future carbon cycle perturbations, comparing a number of emission scenarios and model versions with each other and with zero-dimensional equivalents of each experiment. Overall, we found that our twodimensional weathering model versions were more efficient in restoring the carbon cycle to its pre-industrial state following the pulse emissions than their zero-dimensional counterparts; however, the effect of this weathering negative feedback on the global carbon cycle was small on timescales of less than 1000 years. According to model results, the largest contribution to future changes in weathering rates came from the expansion of tropical and mid-latitude vegetation in grid cells dominated by weathering-vulnerable rock types; changes in temperature and river runoff had a more modest direct effect. Our results also confirmed that silicate weathering is the only mechanism that can lead to a full recovery of the carbon cycle to pre-industrial levels on multi-millennial timescales.

Thirdly, we apply the new weathering parameterization once again to the investigation of future climate changes, but this time following scenarios of representative carbon pathways as presented in the latest IPCC reports. Following on an earlier study which examined the millennial implications of global warming on sea level rise, we come up with a revised assessment of sea level rise taking into account the effect of increased weathering rates on global climate recovery. Based on our model results and interpretation of the impact of temperature on ice sheet melting and sea level rise, we surmise that the impact of rock weathering will not be fast enough to prevent excessive melting of polar ice caps during the next several millennia despite bringing about a much quicker recovery of atmospheric CO_2 levels and surface air temperature to pre-industrial levels.

ABRÉGÉ

Cette thèse présente une série d'études de modélisation climatique portant sur l'interaction entre le climat et l'altération chimique. Le modèle de complexité intermédiaire de l'Université de Victoria (UVic ESCM) est employé pour simuler les variations climatiques, et il est couplé à plusieurs séries de paramétrages de l'altération chimique. Deux périodes importantes de l'histoire climatique de la Terre sont étudiées dans le but d'examiner l'importance du mécanisme de rétroaction de l'altération chimique sur le climat. Premièrement, nous nous tournons vers la plus récente période de fonte glaciaire (approx. 16 000 - 4000 AEC) avec quatre différents paramétrages de l'altération chimique. Le changement climatique déglaciaire dans le modèle est porté par les changements de paramètres orbitaux, de la concentration de dioxyde de carbone dans l'atmosphère, ainsi que la fonte des glaciers continentaux. Durant les quelque 12 000 ans de la simulation, l'augmentation du taux d'altération chimique fournit un mécanisme qui réduit lentement mais sûrement la concentration de CO₂ dans l'atmosphère. Ces processus auraient transféré à la fois du carbone de de l'alcalinité aux océans, dont l'effet combiné aurait été d'augmenter la quantité de carbone dans l'océan de près de 1000 Pg C. L'expansion rapide de la végétation dans l'hémisphère nord introduit une certaine incertitude quant aux paramétrages de l'altération chimique.

Deuxièmement, nous décrivons le développement et l'application d'un nouveau modèle bidimensionnel de l'altération chimique, toujours avec l'UVic ESCM. Ce modèle intègre une base de données moderne de la distribution lithologique sur la surface de la Terre, et l'impact des propriétés physiques et chimiques des différents types de roches sur le taux d'altération chimique permet de définir celle-ci localement sur toutes les unités spatiales du modèle. Notre paramétrage 2-D inclut également une dépendance sur la température, la productivité primaire de la végétation, ainsi que le taux d'écoulement des rivières. Ce modèle est testé avec des simulations de perturbations futures du cycle du carbone (causées par l'activité humaine présente et future), alors que nous comparons plusieurs scénarios d'émissions anthropogéniques entre notre version 2-D et l'équivalent 0-D de chaque paramétrage. En général, le modèle d'altération chimique 2-D s'avère plus efficace à réduire le montant de carbone dans l'atmosphère que la

version 0-D du modèle. Cependant, il demeure que le mécanisme de rétroaction de l'altération chimique a très peu d'effets sur une échelle temporelle de 1000 ans ou moins. Selon les résultats du modèle, les changements les plus importants à l'altération chimique proviennent de changements à la végétation terrestre dans les régions tropicales et tempérées dont le sol rocheux est composé principalement de types rocheux plus vulnérables à l'érosion et l'altération chimique. Nos résultats confirment également que seuls les augmentations du taux d'altération chimique des roches silicates peuvent permettre à la Terre de pleinement retrouver les conditions préindustrielles.

Contributions of Authors

Chapters 3 to 5 of this thesis are in the form of manuscript articles. Chapter 3 has been accepted for publication in **FACETS**, Chapter 4 has been submitted to the journal **Earth System Dynamics**, and Chapter 5 is in preparation for an eventual submission to **Geophysical Research Letters**. The results presented in these manuscripts originate from the research I conducted as part of my Ph.D. studies. The co-authors of these papers, Prof. L. A. Mysak and Prof. H. D. Matthews, provided supervision of the research project and helped edit of the written material. To be specific, L. A. Mysak initiated the thesis research project by suggesting the development of a two-dimensional weathering module for the UVic Model, and provided initial funding for the project. H. D. Matthews provided funding for the past three and a half years, and provided me with assistance in using the model as well as in interpreting the results.

Statement of Originality

Chapter 3 describes the application of a set of box-model weathering parameterizations to an investigation of climate-weathering interactions during the last deglacial period. Although the parameterizations themselves are taken from an earlier study, the manuscript advances the science in several ways:

- I. It is the first investigation of weathering changes during the last deglacial period with the UVic model, and presents the first set of transient runs incorporating rock weathering as a dynamic component of the carbon cycle.
- II. Although the weathering parameterizations themselves are zero-dimensional, many model outputs which are used to drive weathering changes in particular surface air temperature and vegetation productivity (which influence weathering rates in the model)
 are spatially explicit, allowing for a better insight into the spatial distribution of weathering changes.
- III. It quantifies the strength of the weathering feedback mechanism by calculating changes in atmospheric carbon dioxide concentration due to the changes in weathering rates. The individual effects of changes in ocean DIC and alkalinity are separated, revealing the sensitivity of the model output to the rock type fractionation between carbonate-dominant and silicate-dominant weathering.

In Chapter 4, the UVic ESCM is expanded with the incorporation of a new spatially-explicit weathering scheme. New contributions from Chapter 4 are as follows:

- I. A new terrestrial rock weathering scheme is introduced, which takes into account the lithological distribution across the globe and spatially-explicit changes in temperature, vegetation productivity and runoff.
- II. The parameterization of vegetation productivity is modified to prevent rare cases where an infinitesimally low initial primary productivity is increased to orders of magnitude

comparable with other productive areas, thus increasing local weathering by an unreasonable margin.

- III. Model simulations of future climate changes are compared between zero-dimensional and two-dimensional versions of the weathering scheme.
- IV. Model output from the spatially-explicit weathering scheme is consistent with other model studies incorporating a two-dimensional model.

In Chapter 5, we use the weathering scheme introduced in Chapter 4 to re-visit the problem of estimating the amplitude of sea-level rise in the next several thousand years. New contributions from Chapter 5 consist essentially of providing a new insight on future changes in global sea level by taking the weathering negative feedback mechanism into account.

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Chapter 1 Introduction

The study of the nature and causes of spatial and temporal variations in climate has involved many scientists over the course of the last century, and investigations of future global climatic changes and their implications on human society are increasing in number every year. Many Earth scientists focus on the study of paleoclimates, not only in order to explore the rich history of Earth's climatic evolution, but also as a means to better understand the dynamics of our world by relating past climatic phenomena to similar occurrences in present-day or near-future climatic conditions.

The past few decades have also seen a considerable improvement of the research tools used for climate studies, leading to the emergence of international efforts to document and describe various events or periods in the Earth's climatic history. While some investigators reconstruct information about the Earth's past by drilling ice cores or deep ocean sediment cores, others rely on the data supplied by these proxies in ice cores to develop empirical or theoretical models of the Earth and its climate. From model simulations of the major physical mechanisms and interactions in the Earth climate system, one can learn about the sensitivity of the climate to external forcings. Moreover, climate modelling is better suited to explore the factors which drive climate changes on extended time scales.

The slow variations of atmospheric surface temperatures and CO_2 concentrations are reasonably well known over the course of the past hundreds of millions of years, and more precisely so from the start of the Cenozoic era, 65 My ago. Paleoclimate records reveal that CO_2 concentrations in the atmosphere have been higher than today in much of the Cenozoic, and have followed a decreasing trend during the past 40 million years [*Ruddiman*, 2003]. They also point to a crucial role of the global carbon cycle throughout this period and likely beyond [*Ruddiman*, 2008]. For example, a large addition to atmospheric carbon content (i.e. greenhouse gases) is known to have accompanied – and possibly driven – the rapid warming period known as the Paleocene-Eocene Thermal Maximum [*Zachos et al.*, 2005]. There is also evidence for significant variations of atmospheric CO_2 concentrations during the multiple glaciations documented across the Earth's history, the most recent of which being the glacial-interglacial variations of the current Pleistocene epoch [*Kump and Alley*, 1994]. Additionally, in the wake of ongoing and unprecedented (in terms of rapidity) emissions of greenhouse gases to the atmosphere [*Zeebe*, 2012], the immediate and medium-term future of the Earth system is likely to be dominated by large perturbations to the carbon cycle and their impacts on climatic and environmental changes across the world [*Archer et al.*, 1997; *Eby et al.*, 2009].

Of all the processes which drive the global carbon cycle on geologic timescales, terrestrial weathering is perhaps the only mechanism with a direct negative feedback mechanism on global climatic changes [*Urey*, 1952; *Walker and Kasting*, 1992]. At the molecular level, rock chemical weathering can be defined as the cleavage of bonds in a mineral lattice by a chemical reaction with a weathering agent – usually an organic or inorganic acid dissolved in water – which leads to rock degradation and increased vulnerability to large-scale erosion. Rock weathering products, the most common of which are calcium and bicarbonate ions, are carried away with runoff to rivers and into the ocean and, through their impact on the carbonate cycle of the ocean, play a major role in regulating atmospheric and oceanic chemical composition. In addition, the weathering of silicate rocks results in a net removal of carbon dioxide from the atmosphere which, through its coupling with calcium carbonate deposition and burial in the ocean, becomes the primary sink of carbon on geologic timescales.

The rate at which these processes remove carbon from the atmosphere is sensitive to changes in the environment, and can be correlated with changes in air temperature [*Berner*, 1991], biological productivity [*Lenton and Britton*, 2006] and perhaps more indirectly, river runoff [*Walker and Kasting*, 1992]. An increase in any of these parameters as well as the atmospheric concentration of CO_2 can generally be associated with an increase in global carbon consumption by weathering. This gives rise to a negative feedback mechanism which regulates the global climate over millions of years, and several examples exist in past climate changes which point towards an active and determinant role of weathering. Nevertheless, there have been but very few quantitative assessments of its impacts on carbon cycling and ocean biogeochemistry, and its relevance over time frames of 10^4 years or shorter, particularly in periods of rapid climate change, is still the subject of some debate.

The role of rock weathering in regulating long-term global climate has been well-established by early box-model efforts which linked the rate of atmospheric CO_2 consumption by silicate weathering in changes of atmospheric CO_2 partial pressure. The resulting feedback mechanism was offered as an explanation for the general decreasing trend of atmospheric CO_2 levels on geologic timescales [*Walker et al. 1981, Berner et al. 1983, Berner 1991*]. These early models mostly used atmospheric CO_2 concentration as a broad proxy for environmental and/or climate change, although sometimes the direct effects of temperature and river runoff were also parameterized. These models also integrated weathering as part of a box-model global carbon cycle in order to better understand variations of atmospheric CO_2 concentrations during the Phanerozoic. Later carbon cycle models, notably the various versions of GEOCARB [*Berner*, 1991; *Berner*, 1994; *Berner and Kothavala*, 2001], further improved the weathering parameterizations.

Most of the box-model weathering parameterizations used an approach whereby changes in global weathering intensity throughout a transient model simulation would be computed by modulating a known initial value based on transient changes in model parameters: temperature, CO_2 concentration, vegetation productivity and/or runoff. This approach, although a fairly crude way to constrain weathering changes across the globe, could conveniently avoid the problem of directly calculating global weathering intensity. For this reason, few attempts have been made to explore the spatial variability of rock weathering rates, as they would require – at the very least – an estimation of weathering intensity on each of the land spatial units. This issue has generally been addressed by considering the heterogeneous distribution of lithologies across the world, and using established empirical relationships between weathering intensity and runoff for each lithological classification that is being considered [*Amiotte Suchet et al.*, 1995; *Bluth and Kump*, 1994]. These models were used mainly to estimate the global consumption of atmospheric CO_2 by chemical rock weathering, and have only recently been incorporated in transient climate models.

The present thesis expands on the work of *Meissner et al.* [2012], who first introduced boxmodel parameterizations of weathering to the University of Victoria Earth System Climate Model (henceforth: UVic ESCM), and of *Colbourn et al.* [2013], who incorporated a twodimensional parameterization of weathering into an intermediate-complexity model. In the following chapters, I describe the development of a spatially-explicit weathering scheme for use within the UVic ESCM, and its application to constrain weathering changes and their implications on Earth system dynamics during the last deglacial period (ca. 21,000-10,000 BP) and the next several millennia of anthropogenic global warming. Both are periods of rapid climatic changes accompanied with a large carbon-cycle perturbation, which occur on timescales several orders of magnitude below that at which the weathering negative feedback mechanism is thought to operate.

The thesis is structured as follows. Chapter 2 reviews the relevant literature on topics such as carbonate chemistry and ocean biogeochemistry, the weathering feedback mechanism, investigations of climate-weathering interactions during glacial periods and in future global warming scenarios, as well as the evolution of 0-D and 2-D weathering models throughout the past several decades. Chapter 3 describes a preliminary set of experiments, in which we used a box-model parameterization of weathering developed by *Meissner et al.* [2012] for the UVic ESCM in the context of deglacial climate change. Chapter 4 describes the development of a spatially-explicit weathering scheme for the UVic ESCM and its application towards computing changes in weathering intensity in the context of future climate change scenarios driven by pulse emissions of carbon. Chapter 5 describes an extension of the previous work, in which we use the 2-D weathering model within Representative Concentration Pathways (RCP) [*IPCC*, 2013] in order to estimate sea level changes and the contribution of weathering to global climate changes. Finally, the thesis conclusions are given in Chapter 6. It should be noted that this thesis is written in "manuscript" format; Chapters 3, 4, and 5 are all manuscripts which have either been submitted to a scientific journal for publication, or being prepared for such a submission.

Chapter 2 Literature Review

The role of terrestrial rock weathering in regulating the atmospheric and oceanic chemical composition is complex and often overlooked due to the long timescales over which weathering affects the Earth system. Conceptually, this role is quite simple: the chemical reactions through which rock minerals are dissociated involve the consumption of carbon dioxide, which is supplied from the atmosphere. Thermodynamics indicate that in a warmer, wetter world the rate of these reactions and the associated CO₂ consumption would be enhanced, hence weathering serves as a negative feedback mechanism in the climate system. However, any attempts to quantify the effect of weathering in a changing global climate are met with a number of complications. First, the effect of terrestrial weathering on the Earth system is intricately linked to changes in ocean biogeochemistry, and in particular, to the delicate balance between the downward and upward fluxes of calcium carbonate, which are responsible for maintaining ocean pH at stable levels. In large part, the impact of terrestrial weathering on the global carbon cycle is achieved through the neutralization of carbonic acid in the ocean, allowing it to further uptake CO_2 from the atmosphere. The second complication is that the physical laws which determine the rate of weathering reactions are only understood at the molecular level. Once taking into account the heterogeneous composition of rocks, as well as changes in climate conditions which drive changes in weathering intensity at the macroscopic level, even approximating changes in weathering rates become a challenging task. A third problem is that the slow nature of weathering processes means their full impact can only be assessed over extremely long timescales.

The purpose of this literature review is to gain a better understanding of weathering processes and its relation to global climatic changes. The chapter first discusses in section 2.1 the basic chemistry of weathering reactions and ocean biogeochemistry. Section 2.2 introduces the major works which introduced the negative feedback mechanism, while sections 2.3 and 2.4 expand on climate-weathering interactions during the last deglacial period and for future climatic change, respectively. Finally, section 2.5 presents a synopsis of the major modeling efforts upon which the rest of this thesis is built.

1 On rock weathering and ocean biogeochemistry

An imbalance of carbon in the atmosphere-ocean system is restored in large part by the dissolution of carbon dioxide into the ocean and its chemical neutralization by reactions with seawater and dissolved carbonate ions [*Ridgwell and Zeebe*, 2005]. The carbon contained within terrestrial biota and soils reacts quickly to changes in the carbon dioxide content of the atmosphere, and is not important in the long-term regulation of atmospheric carbon dioxide. Most of the following discussion will focus on the oceanic carbon cycle and its interaction with the atmosphere.

The air-sea exchange of carbon occurs naturally due to a CO_2 partial pressure gradient between the atmosphere and ocean surface layer [*Sarmiento and Gruber*, 2006]. A large fraction of CO_2 entering the ocean is hydrated to form carbonic acid (H₂CO₃), most of which dissociates to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions. The speciation between these three components is determined by the pH of seawater; at typical pH values the distribution of inorganic carbon is dominated by HCO₃⁻ (89%) and CO₃²⁻ (10.5%), with only a small fraction present as free aqueous carbon dioxide [*Zeebe*, 2012]. This allows the oceans to store far more carbon than would be allowed by simply taking into account the pCO₂ gradient between the atmosphere and ocean. In fact, exchanges through the air-sea interface account for as much as 70% of CO₂ uptake into the oceans [*Sarmiento and Gruber*, 2006]. The equilibrium reaction for the neutralization of CO₂ in seawater is typically written as follows:

$$CO_{2(aq)} + H_2O + CO_3^{2-} \leftrightarrow 2HCO_3^{-}$$
 (1)

The collective sum of the carbon concentrations from CO_2 , HCO_3^{-1} and CO_3^{-2} species is called *dissolved inorganic carbon* (DIC), and constitutes the principal carbon reservoir in the ocean. A small fraction is stored in the marine biota and in the form of particulate organic carbon, while sedimentary deposits (mostly CaCO₃) make up the rest. Transport of carbon between the surface and deep layers by ocean mixing alone is relatively slow. The sinking of organic matter and CaCO₃ from surface dwelling marine foraminifera and other calcifying organisms (i.e., the carbonate pump) also constitutes a major source of carbon transfer to the deep layers, and this maintains a slightly positive CO_2 density gradient between the deep and surface layers.

At longer timescales, the oceanic carbonate $(CaCO_3)$ cycle becomes an important factor in atmospheric CO₂ regulation. In the ocean, the precipitation and dissolution of CaCO₃ is controlled by the following equilibrium relation:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_{2(aq)} + H_2O \tag{2}$$

The thermodynamic equilibrium of this reaction depends heavily on the bicarbonate ion concentration as well as the ambient pressure (i.e., the depth from the surface) [*Ridgwell and Zeebe*, 2005]. Precipitation is favorable when CO_3^{2-} concentrations are high (high alkalinity / low acidity) and pressure is low (near-surface), while opposite conditions favor dissolution of CaCO₃. This results in a band of CaCO₃ accumulation on low-depth marine shelves (for example, coral reefs), while deeper layers of the ocean have little or no precipitation with a low calcite saturation level. The level at which carbonate dissolution and precipitation equal one another is called the carbonate compensation depth (CCD), and it follows from equations (1) and (2) that its position is directly affected by oceanic DIC, and pCO₂ in particular. The CaCO₃ sediments also act as a buffer on oceanic carbonate alkalinity ([HCO₃⁻] + 2[CO₃²⁻]), restoring carbonate in response to CO₂ incursions to the ocean and thus preventing a catastrophic acidification of the seawater.

Terrestrial rock weathering, especially the dissolution of carbonate minerals on land, is also a major source of carbonate alkalinity for the ocean surface, and prevents an excessive shoaling of the lysocline in response to major incursions of CO_2 from the atmosphere. In general, rock weathering is characterized by the cleavage of bonds of the mineral lattice by water, often in the presence of an organic or inorganic acid. Carbonic acid (H₂CO₃) is one such secondary weathering agent, acquired from the dissolution in rainwater of atmospheric carbon or the oxic degradation of organic matter in soils. Rock weathering products, including calcium and bicarbonate ions (respectively the most abundant cation and anion in most river waters), can be carried away with runoff to rivers and into the ocean. The reverse of equation (2), which describes calcite sediment dissolution, can also be used as a schematic representation of calcium carbonate layer is balanced by the precipitation and burial of biogenic calcium carbonate (CaCO₃) in the sediments; this can accelerate the transfer of CO₂ between the atmosphere and ocean, but it

does not contribute to a permanent return of carbon to the geologic reservoir [*Ridgwell and Zeebe*, 2005; *Sarmiento and Gruber*, 2006].

A large fraction of rock weathering reactions involves a weakening of chemical bonds in the lattice of silicate minerals on contact with water, whereby hydrogen ions replace positively charged cations (mostly Ca^{2+} and Mg^{2+}) which are bounded to the negatively charged ion (alumino) silicate framework. One of the most common examples is given by calcium silicate hydrolysis, as described by following schematic, irreversible (at Earth surface conditions) reaction [*Ebelmen*, 1845; *Urey*, 1952]:

$$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + H_4SiO_4 + 2HCO_3^-$$
 (3)

This equation represents the weathering of a simple silicate mineral (in our example, wollastonite) into silicic acid (which often precipitates as amorphous silica SiO₂), and consumes one more molecule of CO_2 than carbonate dissolution while sending the same amounts of calcium and bicarbonate ions to the ocean. The combination of equation (3) with calcium carbonate precipitation (forward direction of equation 2) shows how this results in a net removal of one molecule of CO_2 :

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \tag{4}$$

Carbon dioxide consumption due to silicate weathering has been approximated to between 7-12 $\times 10^{12}$ moles per year [*Moon et al.*, 2014] – significantly lower than other carbon cycle fluxes and thus only an important sink of carbon in geologic timescales (10^5 - 10^6 + years). On these timescales the geologic reservoir of carbon becomes active, and it is responsible for the permanent removal of carbon from the Earth system (for example, through the subduction of a sediment shelf back into the mantle) [*Zeebe*, 2012], ultimately balancing the incursion of carbon from geological sources, such as volcanic eruption and anthropogenic fossil fuel burning.

From this point onwards, dissolution of carbonates (on land) and hydrolysis of silicates will be referred to as carbonate and silicate weathering, respectively.

2 The rock weathering negative feedback mechanism

Since the pioneering work of Urey [1952], which first discussed the geochemical importance of silicate rock weathering, it has been believed that the fluctuations of weathering intensity across the globe could play an important part in the regulation of atmospheric CO₂ concentrations on geologic time scales. Meybeck [1979] investigated the history of the dissolved mineral supply to the ocean and established a correlation between rates of silicate rock weathering and many climate parameters such as temperature, precipitation, and the atmospheric partial pressure of CO_2 . Subsequent work linked the rate of atmospheric CO_2 consumption by silicate weathering to changes of atmospheric partial CO₂ pressure and used the resulting feedback mechanism as an explanation for the general decreasing trend of atmospheric CO₂ levels on geologic timescales [for example, Walker et al., 1981; Walker and Kasting, 1983; Berner et al., 1983]. Walker, Hays and Kasting [1981], henceforth referred to as WHAK, developed expressions relating silicate weathering to atmospheric pCO₂ (through vegetation production) and temperature (including a weak dependency on runoff). They used these dependencies to offer a solution to the faint young Sun paradox, pointing out that gradually increasing weathering rates (on average) during the Phanerozoic would have conveniently decreased greenhouse gas concentrations, thus limiting the magnitude of temperature increase from an increasingly brighter Sun. Around the same time, Berner, Lasaga and Garrels [1983], henceforth referred to as BLAG, built a geochemical cycle model in which the long-term evolution of atmospheric carbon content was driven by imbalances between CO₂ outgassing by volcanic activity and the burial of carbonate sediments which follows the weathering of silicate rocks. In this model, the silicate weathering rate was given a similar dependency on temperature and atmospheric CO₂, and it was used to solve a series of mass balance equations in order to determine the inward and outward fluxes for the atmospheric, land, ocean, and mineralogical carbon reservoirs. Although these models used rudimentary parameterizations derived from early general circulation models and experimental data, they established the foundation for future long-term carbon cycle model studies.

An increase in global weathering intensity has often been cited as one of the main factors behind the gradual cooling of the Cenozoic era (c. 65Mya to the present), which led the world from a hothouse to an icehouse climate characterized by permanent land ice at polar latitudes. *Raymo et al.* [1988] argued that tectonic uplift in the mid- to late Cenozoic – notably from the subduction of the Indian plate under the Eurasian plate – became a major source of weathering activity and CO_2 consumption, leading to global cooling. In contrast, *Berner et al.* [1983] (aka. BLAG) linked the rate of atmospheric CO_2 consumption by weathering to changes in surface air temperature, atmospheric partial CO_2 pressure, and river runoff. They offered this dependency as the main driver of CO_2 changes during the Cenozoic and later. It was later determined [*Sundquist*, 1991] that feedbacks between atmospheric CO_2 (and therefore climate) and weathering rates act to maintain the long-term carbon cycle in steady state. *Kump et al.* [2000] further highlighted the carbonate-silicate weathering cycle as a key factor that prevents excessive fluctuations in atmospheric pCO_2 over these time scales. A good example would be the tectonic changes during the current Cenozoic period, which are thought to have driven the gradual cooling trend of the past 55Myr, and for which the role of weathering on CO_2 fluctuations is still poorly understood [*Mills et al.*, 2014].

The 1990s saw the development of perhaps the most influential series of geochemical models, and the first real introduction of weathering as a component in a dynamic Earth system model. Building on the earlier modelling efforts of WHAK and BLAG, Berner [1991] simplified the geochemical component by lumping together all carbonate minerals and combining the atmosphere and ocean into a single reservoir, in favor of adding more direct biological mechanisms (notably, the soil-biological enhancement of weathering). In addition, land area, elevation, and runoff were also introduced as parameters in the new model called GEOCARB. Much like its predecessors, this model was developed in order to reconstruct the evolution of atmospheric pCO₂ over the past hundreds of millions of years, which was approximated as a series of successive atmosphere-ocean steady states. Subsequent versions were called GEOCARB II [Berner, 1994] and GEOCARB III [Berner and Kothavala, 2001], and these further improved the weathering parameterizations based on the latest observational data and GCM output. They were later coupled with a model of atmospheric O_2 and ocean nutrients to create COPSE [Bergman et al., 2004], a multi-element geochemical cycling model which introduces a feedback-based interaction between biotic and abiotic elements of the Earth system. It was also coupled with a long-term sulfur cycle to create GEOCARBSULF [Berner, 2006], a revised model version which also simulates the O_2 cycle.

3 Variations in weathering rates during the Pleistocene icehouse climate

Due to gradually decreasing temperatures throughout the Cenozoic [*Ruddiman*, 2006], the Earth reached a threshold approximately 2 million years ago when air temperatures in the northern continental high latitudes were cool enough to allow ice to persist from one winter to another, thus initiating a cycle of glacial and interglacial periods. The periodicity of glacials (and interglacials) has varied considerably over time, with interglacials occurring on average every 100,000 years in the past million years, and these variations are generally accepted to be caused by changes in the Earth's orbital configuration [*Milankovitch*, 1941] and their impact on high latitude summer insolation. When the combination of orbital parameters results in high summer insolation, ablation during the warm period overcomes winter accumulation and continental ice sheets recede. Conversely, a summer minimum of solar insolation would mitigate summer melting and promote ice sheet growth. This is now commonly known as the astronomical theory of climate [*Hays et al.*, 1976; *Imbrie et al.*, 1980].

Factors known to impact weathering rates during periods of icehouse climate include air temperature, transport rate of minerals, geographical distribution of rocks, vegetation and tectonic uplift [*Kump et al.*, 2000]. In particular, one would expect weathering rates to be drastically reduced during periods of severe continental glaciation considering the much lower global temperatures and the weathering-inhibiting impacts of ice on land [*Kump and Alley*, 1994]. This reinforces the idea that silicate rock weathering should have acted as a negative feedback on the climate system.

The best analog for studying variations in weathering rates during an icehouse climate is the last glacial maximum (LGM), a period of extensive Northern Hemisphere glaciation 21,000 ago during which much of the North American and European continents poleward of 40°N were covered in ice. Concurrent with the increase in land ice was a significant drop in sea level, exposing previously submerged continental shelves, representing as much as a 13% increase of the Earth's continental landmass. The exposed continental shelves – many of which were situated in non-glaciated areas – would have been subject to some weathering, thus increasing the global amount of weathering [*Kump and Alley*, 1994]. Interestingly enough, these shelves tended to appear preferentially in the tropics, in particular the Indonesian basin where high

temperature and rainfall would be conducive to high rock weathering rates. Additionally, geological surveys reveal a very heterogenic distribution of rocks around the globe: carbonaterich limestones tend to be more aggregated in tropical regions, and would thus have been more exposed to weathering during the LGM, whereas silicate rocks are more evenly spread, hence subject to a potentially significant reduction in exposure at peak glacial periods. However, the loss in exposure mainly occurs at high latitudes, where weathering rates are lower due to a generally colder and drier climate in these regions. As a result of the above factors, bicarbonate production from carbonate weathering would have increased by 20% during the LGM [Gibbs and Kump, 1994], whereas CO₂ consumption from silicate weathering possibly decreased by as much as 10% [Ludwig et al., 1999]. Moreover, high erosion rates coupled with low weathering act to increase the mineral reactivity of silicate rocks, making them more susceptible to changes in the above factors, drastically increasing weathering rates during the subsequent deglaciation [Kump and Alley, 1994]. The combination of these factors gives a fairly inconclusive insight on whether weathering rates are positively or negatively impacted by a shift to glacial conditions in the Northern Hemisphere. More recent studies [Foster and Vance, 2006; Uchikawa and Zeebe, 2008; Zeebe and Caldeira, 2008; Brovkin et al., 2012] suggest that weathering rates were not significantly different at the LGM than they are in the modern day.

There are few published attempts in the literature to explore the potential of climate models in resolving the variations in chemical weathering rates during the Pleistocene icehouse climate. In an intercomparison study, *Munhoven* [2002] examined glacial-interglacial variations in CO₂ with two global weathering models. He found that bicarbonate production rates decreased by 20-30%, whereas CO₂ consumption rates decreased by 5-20% during the LGM. However, this loss in CO₂ consumption was not partitioned equally between the two weathering processes. The models displayed a decrease in silicate weathering rates by 0.7 Tmol/yr, while carbonate weathering rates increased by 3.4 Tmol/yr. These changes in CO₂ consumption rates accounted for 11-26% of total fluctuations in atmospheric CO₂ levels. Another study that used the global climate model CLIMBER [*Brovkin et al.*, 2012] examined a large array of climatic feedbacks during glacial conditions. Based on the model output, they reasoned that a substantial fraction of changes in carbonate chemistry was directly attributable to changes in carbonate weathering. Changes in silicate weathering rates were less pronounced as most of it happens in continental interiors.

4 Weathering and the fate of anthropogenic CO₂

Evaluating the consequences of anthropogenic CO_2 emissions for the twenty-first century and beyond is a major topic in climate research, and the subject of a heated political debate. To date, human activity has resulted in the emission of over 330 Pg of carbon into the atmosphere, mainly through fossil fuel combustion in the past 150 years [*Meissner et al.*, 2012]. This has led to an increase in atmospheric CO_2 concentration of 40% above pre-industrial levels. Modern-day CO_2 levels of over 400 ppm exceed any of those in the past 20-30 million years [*Zachos et al.*, 2008], and the rate at which carbon accumulates in the atmosphere is likely higher than it has been in all of Earth's history.

Theoretical studies on the lifetime of anthropogenic climate change introduce a range of possible future carbon emission scenarios and use carbon-cycle models (often coupled to simple or intermediate-complexity climate models) to assess the evolution of atmospheric CO_2 levels over a timescale of several centuries to a few millennia [see, for example, *Archer et al.*, 1997; *Lenton and Britton*, 2006; *Ridgwell et al.*, 2007; Eby *et al.*, 2009]. Oceans are the primary sink of atmospheric CO_2 on almost all significant timescales [*Eby et al.*, 2009]; nevertheless, they cannot be considered as a panacea for a short CO_2 residence time (i.e., not more than a few 100 years) in the atmosphere, as other processes must act to evacuate carbon from the oceans before it can take up more from the atmosphere [*Brovkin et al.*, 2008]. In fact, climate model simulations show that the timescale of recovery is highly dependent on the total amount of carbon released into the atmosphere. For example, *Eby et al.* [2009] calculate that for total emissions of less than 1000 Pg, most of the CO_2 anomaly is absorbed within 1000 years; however, for a carbon amount equivalent to the known reserves of fossil fuels (about 5000 Pg C), it would take over 2000 years for the oceans to take up only half of the anomaly, and up to several hundreds of thousands of years for it to dissipate completely.

Recent decades of research have shown that CO_2 is removed from the atmosphere in various geochemical pathways [*Archer et al.*, 1997]. Neutralization by seawater brings ocean and atmospheric pCO₂ into equilibrium with each other on timescales of several centuries to a few millennia. However, large uptakes of atmospheric CO_2 create an imbalance in the carbon chemistry of the oceans, causing them to become increasingly acidic and less able to absorb carbon. On millennial time scales, two independent processes act to restore seawater chemistry: the dissolution of seafloor carbonates resulting from a decrease in the carbonate compensation depth (i.e., lysocline shoaling), and the dissolution of terrestrial carbonates as a result of continental rock weathering. In their pioneering work on the rock cycle, *Walker and Kasting* [1992] determined that in the case of greenhouse-induced global warming the enhancement of carbonate weathering on land would have a greater impact on CO_2 drawdown from the atmosphere than the dissolution of marine carbonate sediments. This result was corroborated by later studies; in particular, *Lenton and Britton* [2006] found that the increase in alkalinity to the oceans from carbonate weathering would remove 9-15% of anthropogenic carbon from the atmosphere, while sea-floor neutralization only accounted for 3-8% of CO_2 drawdown (these percentages increase for greater values of CO_2 emissions). They also determined that CO_2 emissions of over 7350 Gt would be necessary to cause the dissolution of all carbonate sediments, which shows the extent of this oceanic buffer factor.

In most coupled carbon cycle-climate simulations, about 7-11% of anthropogenic carbon remains in the atmosphere even when considering seawater and sea-floor neutralization on multimillennial timescales [*Archer et al.*, 1997; *Lenton and Britton*, 2006; *Archer and Brovkin*, 2008]. This anomaly is caused by an imbalance of carbon between the ocean-atmosphere system and the lithosphere; it can only be removed by silicate rock weathering on geologic timescales. This effectively means that the legacy of human-induced climate change could last for several hundreds of thousands of years.

A number of studies have addressed the consequences of anthropogenic carbon emissions and the multi-millennial lifetime of its perturbation on the climate system. The early literature generally agrees on an e-folding timescale on the order of 10^5 years [*Sundquist*, 1991], with values of 200 kyr [*Archer et al.*, 1997] and 400 kyr [*Berner and Kothavala*, 2001; *Archer*, 2005] most often cited. Most recent work on this topic [*Ridgwell and Hargreaves*, 2007; *Montenegro et al.*, 2007; *Uchikawa and Zeebe*, 2008; *Archer et al.*, 2009; *Eby et al.*, 2009] has involved intermediate-complexity models, which are usually limited in scope to run 10^4 years or shorter. Hence the weathering feedback mechanism in these studies is limited to the pH neutralization effect of carbonate weathering on the oceans (which restores the lysocline to its original depth), and with very few exceptions (see *Colbourn et al.* [2015]), silicate weathering is either ignored altogether or prescribed as a global constant average flux.

In a pioneering study, Walker and Kasting [1992] considered the impact of the rock cycle and carbonate sediment dissolution in projections of future changes in the global carbon cycle. Their model was built on the assumption that the dependency of carbonate and silicate weathering rates on changes in the carbon cycle (atmospheric CO_2 levels) was purely abiotic, which was in line with the other geochemical cycling models of the time. Following on Walker and Kasting [1992] as well as the recent innovations in COPSE, Lenton and Britton [2006] posited that biological changes in the Earth system could further enhance the increase or decrease in rock weathering rates, especially in the context of a rapidly warming world which would result from unabated anthropogenic emissions. Their carbon cycle model included sophisticated biotic and abiotic transports of carbon, and it introduced a box-model representation of carbonate and silicate weathering processes in which weathering rates were directly dependent on plant productivity, rather than on atmospheric CO₂ concentrations. This allowed them to investigate the role of land use changes on the long-term recovery of atmospheric CO₂; in particular, they found that vegetation-suppressing land use changes would force CO₂ levels to stabilize above preindustrial levels on geologic timescales, thus indefinitely trapping some of the anthropogenic emissions in the atmosphere.

5 Models of terrestrial weathering

Although rarely present in intermediate complexity climate system models due to their relatively small short-term impacts, weathering processes have been part of several carbon-cycle models that are used to investigate interactions with the climate system on extended time scales. Weathering rates (and the processes involved therein) are calculated as part of the input of biogeochemical quantities to the ocean from river discharge, usually based on the flux of alkalinity and inorganic carbon (i.e., DIC) to the oceans. These are often parameterized as a function of carbon dioxide levels, surface air temperature, plant primary productivity, or any combination of the above. The exact formulation varies among the different carbon-cycle models.

Of the different weathering schemes developed over the decades, two are widely cited in the literature. The first one was developed by *Walker and Kasting* [1992] as part of a carbon cycle box model built in order to evaluate the relative importance of the rock cycle and plant biomass

on future levels of atmospheric CO₂. The parameterization of carbonate and silicate weathering processes is based on the original formulation by *Walker et al.* [1981], which proposes a relationship in the order of $(W/W_0) = (pCO_2/pCO_{2,0})^{0.3}$, where *W* is the weathering flux, pCO_2 the partial pressure of CO₂ in the atmosphere, and the index 0 indicates present day values. The model by *Walker and Kasting* [1992] introduce separate carbonate and silicate weathering:

$$\frac{F_{Alk,w}}{F_{Alk,w,0}} = f_{Si} \left(\frac{pCO_2}{pCO_{2,0}}\right)^{nSi} + f_{Ca} \left(\frac{pCO_2}{pCO_{2,0}}\right)^{nCa}$$
(5)

$$\frac{F_{DIC,W}}{F_{DIC,W,0}} = f_{Si} + f_{Ca} \left(\frac{pCO_2}{pCO_{2,0}}\right)^{nCa}$$
(6)

where $F_{Alk,w}$ and $F_{DIC,w}$ represent the alkalinity and inorganic carbon inputs to the oceans from rock weathering, f_{Si} and f_{Ca} the respective proportions of silicate and carbonate weathering in the total weathering flux, and nSi and nCa are power laws which differ in various applications of the model. For example, the original version of the model uses nCa = 1.0 and nSi = 0.3 as per the work of *Walker et al.* [1981]. On the other hand, *Uchikawa and Zeebe* [2008] set these parameters to 1.0 and 0.6, respectively, and *Zeebe et al.* [2008] used 0.4 and 0.2 respectively. The formulation of equations (5) and (6) used here is derived from *Meissner et al.* [2012].

The second set of parameterizations is the one included in the carbon-cycle model GEOCARB II [*Berner*, 1994] and subsequent versions, which has been used in various complexities of climate models. This model differs from that of *Walker and Kasting* [1992] by adding a temperature dependency and a slightly altered parameterization of CO_2 effects. Similarly to the previous model, the results of rock weathering are incorporated as a flux of alkalinity and dissolved inorganic carbon to the oceans:

$$\frac{F_{Alk,w}}{F_{Alk,w,0}} = g_{CO_2}(CO_2) \cdot [f_{Si} \cdot g_{Si}(SAT) + f_{Ca} \cdot g_{Ca}(SAT)]$$
(7)

$$\frac{F_{DIC,w}}{F_{DIC,w,0}} = f_{Si} + f_{Ca} \cdot g_{CO_2}(CO_2) \cdot g_{Ca}(SAT)$$
(8)

where

$$g_{CO_2}(CO_2) = \left(\frac{2\frac{pCO_2}{pCO_{2,0}}}{1 + \frac{pCO_2}{pCO_{2,0}}}\right)^{0.4}$$
(9)

$$g_{Si}(SAT) = (1 + 0.038(SAT - SAT_0))^{0.65} e^{0.09(SAT - SAT_0)}$$
(10)

$$g_{Ca}(SAT) = 1 + 0.087(SAT - SAT_0)$$
(11)

and other parameters are as presented above, as per the formulation of *Meissner et al.* [2012]. As in the model of *Walker and Kasting* [1992], changes in carbonate weathering affect both the alkalinity and DIC input to the ocean, while changes in silicate weathering only have an impact on alkalinity discharge (as the only net output of carbon takes the form of calcium carbonate, see equation 4). The exponential dependence of silicate weathering rates on temperature is determined empirically from data presented in the works of *Lagache* [1965, 1976] and *Meybeck* [1979], while the linear dependence is derived from parameter adjustment. An alternate version of this model was developed by *Lenton and Britton* [2006], who proposed to replace the dependence on atmospheric CO₂ with plant productivity (NPP). In their formulation, appearances of $g_{CO_2}(CO_2)$ are replaced by $(\frac{NPP}{NPP_0})$, where *NPP* is the global net primary production.

There are very few applications of the above weathering parameterizations outside of carboncycle box models. Intermediate complexity (including the UVic ESCM) models define the weathering rates according to the other fluxes of carbon in and out of the lithosphere (e.g., sedimentation, volcanism) such that the carbon cycle is in steady state over tectonic timescales. Of course, this does not account for weathering adjustment due to climate change, and thus the negative feedback described in *Walker et al.* [1981] is effectively inhibited. In an attempt to restore this feedback mechanism in the UVic model, *Meissner et al.* [2012] examined the impact of continental weathering on atmospheric CO_2 evolution in a simulation of human-induced future climate change. Their study employed five different parameterizations derived from the formulations of *Walker and Kasting* [1992] and *Berner* [1994]. In addition they carried out simulations with constant alkalinity and DIC discharge rates. They found that the parameterization of *Walker and Kasting* [1992], which depends solely on atmospheric CO_2 produces a stronger negative feedback than the other parameterizations. The formulation of Lenton and Britton [2006], the only one to use plant productivity as a factor, produces the most similar results. In the simulation with constant weathering rates, the atmosphere retains almost twice as much CO_2 than in other simulations where weathering rates are susceptible to climate change. Since the temperature response lags behind the CO_2 curve, the difference between simulations with a temperature dependency and those without is more pronounced in higher emission scenarios. *Meissner et al.* [2012] also confirmed the results from *Uchikawa and Zeebe* [2008] that weathering only becomes a significant feedback over timescales exceeding several millennia, and the findings of *Eby et al.* [2009] that the CO_2 response is largely independent of the rate at which it is emitted in the atmosphere.

Few attempts have been made to explore the spatial variability of carbonate and silicate weathering rates and how it may affect the global efficacy of the weathering negative feedback mechanism. The main problem relating to the development of spatially explicit weathering schemes is the necessity to compute weathering individually for each land grid cell, which is entirely more complex than using a globally-averaged value, for which many precedents exist in the literature. The GEM-CO₂ model [*Amiotte Suchet and Probst*, 1995] addressed this problem by defining the spatial variability in terms of rock types, and using data for bicarbonate (HCO₃⁻) concentration and runoff collected over various mono-lithologic drainage basins [*Meybeck*, 1987] to establish empirical linear relationships between weathering flux and runoff for a series of major rock types. Arguing that these two factors (runoff and rock type) were the main factors controlling the consumption of atmospheric/soil CO₂ by weathering, they calculated the global distribution of CO₂ consumption. Their results showed a higher intensity of weathering in the Northern Hemisphere (due to rock type) and in equatorial regions (due to runoff).

Amiotte Suchet et al. [2003] refined the global distribution of rock types by attributing one of six rock types to each land unit of a $1^{\circ} \times 1^{\circ}$ grid [Amiotte Suchet et al., 2003]; this distribution will be used as the basis for our spatially explicit weathering scheme. Rock types, from having the smallest to largest impact on weathering, are classified as follows: plutonic and metamorphic (shield) rocks, sands and sandstones, extrusive igneous (acid volcanic) rocks, basalts, shales and evaporites, and carbonate rocks. The latter group consists of predominantly carbonate-based rocks, and of the other five rock types only sandstones and shales contain a fraction of carbonate-weathered minerals. In the other rock types, the prevalence of carbonate minerals is too variable
and difficult to estimate; hence they are assumed to contain only silicate-weathered minerals. Using the GEM-CO₂ model, carbonate rocks and shales were found to both consume 40% of the total continental CO₂ uptake despite occupying a much smaller fraction of land area, while sandstones and shield rocks contributed much lower than their outcrop abundance. A similar rock type distribution was developed [*Gibbs and Kump*, 1994; *Bluth and Kump*, 1994] (hence GKWM), using both an empirical linear coefficient and an exponential factor to express weathering dependence on runoff for different rock types; however the results produced by their lithological distribution was found to be very similar to that of GEM-CO₂ in terms of global weathering intensity and the consumption of atmospheric/soil CO₂ [*Colbourn et al.*, 2013; *Colbourn et al.*, 2015].

Other instances of spatially-explicit weathering models are few in the literature. The GEOCLIM model has a built-in two-dimensional weathering scheme that has been used to investigate the climatic impacts of tectonic continental reorganization and weathering-vegetation interactions [*Donnadieu et al.*, 2009]. More recently, a spatially-explicit scheme was added to the GENIE model [*Colbourn et al.*, 2013]. These authors used lithological databases from the GEM-CO₂ and GKWM models, temperature dependency from the GEOCARB models, NPP dependency as introduced by *Lenton and Britton* [2006], and runoff dependency from GEM-CO₂. Although the paper focused mostly on exploring the various model options, the authors were able to simulate the entirety of the climate system recovery from a 5000 Pg C anthropogenic pulse at year 2000, showing that within 0.5-1 Myr the atmospheric CO₂ levels would return to pre-industrial levels.

Chapter 3

Carbon cycle implications of terrestrial weathering changes since the last glacial maximum

Previous studies [*Kump and Alley*, 1994; *Bluth and Kump*, 1994] suggest that weathering changes during the last deglacial period may have been significant enough to have a non-negligible impact on atmospheric CO_2 levels during this period of relatively rapid global warming. Using the box-model parameterizations of *Meissner et al.* [2012] which have already been incorporated into the UVic model, we simulate deglacial climate change and the associated effects on global weathering intensity, and subsequently use the changes in weathering rates to estimate their impacts on atmospheric CO_2 concentrations. This chapter is based on a paper by authors Brault, M.-O., Mysak, L.A., and Matthews, H.D., which has been accepted for publication in FACETS.

Carbon cycle implications of terrestrial weathering changes since the last glacial maximum

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ABSTRACT

We examine the importance of the rock weathering feedback mechanism during the last deglacial period (ca. 16,000 - 4,000 BCE) using an Earth system model of intermediate complexity (the UVic ESCM) with four box-model parameterizations of terrestrial weathering. The deglacial climate change is driven by changes in orbital parameters, ice-core reconstructions of atmospheric CO₂ variability, and prescribed removal of continental ice sheets. Over the course of the 12,000-year simulation period, increases in weathering provide a mechanism that slowly removes CO₂ from the atmosphere, in opposition to the observed atmospheric CO₂ increase during this period. These processes transfer both carbon and alkalinity to the ocean, the combination of which results in as much as a 1000 Pg C increase in total ocean carbon, relative to a control simulation with constant weathering. However, the rapid expansion of northern Hemisphere vegetation introduces a significant uncertainty among the weathering parameterizations. Further experiments to test the individual impacts of weathering dissolved inorganic carbon and alkalinity fluxes on ocean biogeochemistry suggest that the worldwide distribution of rock types and the ratio of carbonate to silicate weathering may be crucially important in obtaining an accurate estimate of changes in global weathering rates.

1 Introduction

The weathering of carbonate and silicate rocks on land is a key process in the global carbon cycle and, through its coupling with calcium carbonate deposition in the ocean, is the primary sink of carbon on geologic timescales [*Urey*, 1952; *Walker et al.*, 1981]. The rate at which these processes remove carbon from the Earth system is sensitive to changes in the environment, notably temperature [*Berner*, 1991], biological production [*Lenton and Britton*, 2006] and perhaps more indirectly, river runoff [*Walker and Kasting*, 1992]. This gives rise to a negative feedback mechanism which regulates the global climate on multimillennial time scales. However, there have been very few quantitative assessments of its impacts on carbon cycling and ocean biogeochemistry, and its relevance over time frames of 10^4 years or shorter is largely unknown.

The purpose of this paper is to investigate how the potential changes in global terrestrial weathering may have affected ocean biogeochemistry and the global carbon cycle during the last deglacial period (ca. 19,000-4000 BC). Changes in weathering rates are expressed as a modulation of initial conditions based on changes in temperature, atmospheric CO_2 , or vegetation net primary production, and various parameterizations are tested and compared using the University of Victoria Earth System Climate Model (UVic ESCM). A prescribed time series of atmospheric CO_2 is used to accurately drive climate change during the period and thus better estimate changes in weathering rates. The impact of the latter on atmospheric CO_2 concentrations is then determined by using the weathering rates obtained previously as boundary conditions for a second set of simulations performed at various periods of the deglaciation during which atmospheric CO_2 is allowed to vary according to model carbon cycle dynamics. Overall, this study allows us to make an estimate of the variations in weathering rates within glacial-interglacial timescales and their impact on the carbon cycle.

The chemical weathering of rocks is characterized by the cleavage of bonds of the mineral lattice by water, often in the presence of an organic or inorganic acid. Carbonic acid (H_2CO_3) is one such secondary weathering agent, acquired from the dissolution in rainwater of atmospheric carbon or the oxic degradation of organic matter in soils. Rock weathering products, including calcium and bicarbonate ions (respectively the most abundant cation and anion in most river waters), can be carried away with runoff to rivers and into the ocean. For example, calcium carbonate dissolution by carbonic acid is represented by:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$
 (1)

The influx of dissolved inorganic carbon ($[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$, henceforth DIC) and carbonate alkalinity ($[HCO_3^-] + 2[CO_3^{2-}]$, henceforth CA) to the ocean surface layer is balanced by the precipitation and burial of biogenic calcium carbonate (CaCO₃) in the marine sediments; perturbations to the oceanic $[CO_3^{2-}]$ (= (CA – DIC) at the pH of seawater) result in a repositioning of the carbonate compensation depth (CCD), the depth below which the dissolution rate of calcium carbonate exceeds its flux to the deep sea. In the long term, this allows the ocean to maintain a remarkably stable alkalinity, as any increases in ocean acidity (such as can be caused by a CO₂ invasion from the atmosphere) can be neutralized by elevating the CCD, exposing carbonate sediments to dissolution and the release of carbonate ions (CO_3^{2-}) back into This oceanic buffer factor, along with carbonate dissolution on land (due to the ocean. weathering), is the primary means through which ocean alkalinity is restored, and is responsible for maintaining both atmospheric and oceanic pCO₂ close to equilibrium. In short, the weathering of calcium carbonate can accelerate the transfer of CO₂ between the atmosphere and ocean, but does not contribute to a permanent return of carbon to the geologic reservoir [Ridgwell and Zeebe, 2005; Sarmiento and Gruber, 2006].

A large fraction of rock weathering reactions involves a weakening of chemical bonds in the lattice of silicate minerals on contact with water, whereby hydrogen ions replace positively charged cations (mostly Ca^{2+} and Mg^{2+}) which are bounded to the negatively charged ion (alumino)silicate framework. One of the most common examples is given by calcium silicate hydrolysis, as described by following schematic, irreversible (at Earth surface conditions) reaction [*Ebelmen*, 1845; *Urey*, 1952]:

$$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + H_4SiO_4 + 2HCO_3^-$$
 (2)

This equation represents the weathering of a simple silicate mineral (in our example, wollastonite) into silicic acid (which often precipitates as amorphous silica SiO_2), and consumes one more molecule of CO_2 than carbonate dissolution while sending the same amounts of calcium and bicarbonate ions to the ocean. The combination of equation (2) with calcium

carbonate precipitation (the reverse of equation 1) shows how this results in a net removal of one molecule of CO₂:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \tag{3}$$

Weathering rates due to silicate hydrolysis tend to be considerably slower than from the dissolution of carbonate minerals – it removes on average 0.28 to 0.30 Pg C per year [*Amiotte Suchet and Probst*, 1995] – hence the effect of atmospheric CO₂ consumption by silicate weathering only becomes a significant sink of carbon on geologic timescales ($10^{5}-10^{6}+$ years). For the remainder of this article, dissolution of carbonates (on land) and hydrolysis of silicates will be treated separately and referred to as carbonate and silicate weathering, respectively.

The role of rock weathering in regulating long term global climate has been established by past box-modeling efforts [*Walker et al. 1981, Berner et al. 1983, Berner 1991*]. These studies linked the rate of atmospheric CO_2 consumption by silicate weathering to changes in atmospheric partial CO_2 pressure, as a possible explanation for the general decreasing trend of atmospheric CO_2 levels on geologic timescales. Although atmospheric CO_2 concentration is often used as a broad proxy for environmental and/or climate change, sometimes the direct effects of temperature and river runoff were also parameterized. *Walker, Hays and Kasting* [1981], henceforth referred to as WHAK, developed expressions relating silicate weathering to atmospheric pCO_2 (through vegetation production) and temperature (including a weak dependency on runoff) and used them to offer a solution to the faint young Sun paradox by providing a convenient mechanism for a slow and steady decrease in atmospheric greenhouse gas concentrations. Although the model used rudimentary parameterizations derived from early general circulation models and experimental data, it built a foundation for future long-term carbon cycle model studies.

Berner, Lasaga and Garrels [1983], henceforth referred to as BLAG, built a geochemical cycle model in which the long-term evolution of atmospheric carbon content is driven by imbalances between CO_2 outgassing by volcanic activity and the burial of carbonate sediments which follows the weathering of silicate rocks. In this model, the silicate weathering rate was given a similar dependency on temperature and atmospheric CO_2 , and it was used to solve a series of mass balance equations in order to determine the inward and outward fluxes for the atmospheric, land, ocean, and mineralogical carbon reservoirs. Following BLAG, Berner [1991] simplified the geochemical component by lumping together the carbonate minerals and combining the atmosphere and ocean into a single reservoir, in favor of adding more direct biological mechanisms (notably, the soil-biological enhancement of weathering). Land area, elevation, and runoff were also introduced as parameters in the new model called GEOCARB. Much like its predecessor, this model was developed in order to reconstruct the evolution of atmospheric pCO₂ over the past hundreds of millions of years (which was calculated as a series of successive atmosphere-ocean steady states). Subsequent versions were called GEOCARB II [*Berner, 1994*] and GEOCARB III [*Berner and Kothavala,* 2001], and these further improved the weathering parameterizations based on the latest observational data and GCM output.

The importance of the negative feedback mechanism associated with rock weathering is somewhat underwhelming on non-geologic time scales, with few notable exceptions; chief among these is the late Pleistocene epoch [Kump and Alley, 1994; Munhoven, 2002] because of the rapid climatic and environmental changes which accompany glacial inception and termination. Yet due to a lack of a quantitative assessment of the latter's impacts on global rock weathering, there is considerable uncertainty as to whether the intensity of each glacial or interglacial period would be reinforced or tempered as a result of changes in weathering rates [Bluth and Kump, 1994]. On the one hand, the combination of cooler global temperatures and weathering-inhibiting ice sheets should act to reduce CO₂ consumption from chemical weathering during glacial maxima, hence keeping with its perceived role as negative feedback mechanism. On the other hand, the drop in mean sea level during said glaciations would have increased the effective area of continental shelves which are exposed to weathering, including a large increase in continental land area at low latitudes. Moreover, the intense pressure of ice sheets could increase the mineral reactivity of silicate rocks, thus drastically increasing weathering rates for a short period when the ice sheet retreats and the area is subject to weathering again [Kump and Alley, 1994]. However, little is known about the relative impacts of each of those factors; thus it is difficult to establish with certainty what would have been the role of rock weathering in the context of shifting glacial conditions in the Northern Hemisphere.

Few attempts have been made using climate models to investigate the significance of variations in chemical weathering rates during the Pleistocene glacial cycles. *Bluth and Kump* [1994]

developed a spatially-explicit, empirical weathering scheme in which the runoff dependency of weathering is modulated by the local lithological composition. Considering an increase of continental margins and a decrease in ice-free continental land during the LGM, this model could not reproduce the apparent increase in global silicate weathering that was suggested by the Ge/Sr isotope records of that time [*Gibbs and Kump*, 1994]. In an intercomparison study, Munhoven [2002] compared glacial-interglacial variations in CO₂ between the latter and GEM-CO₂ [*Amiotte Suchet and Probst*, 1995] models. Glacial bicarbonate production rates were found to be 20-30% lower compared to the present day, whereas CO₂ consumption rates decreased by 5-20% during the LGM, accounting for up to one quarter of the total fluctuations in atmospheric CO₂ levels. The loss in CO₂ consumption was not partitioned equally between the two weathering processes, with a slight increase in modern silicate weathering being accompanied by a much larger decrease in carbonate weathering. More recently, the importance of rock weathering on glacial timescales has been questioned; *Foster and Vance* [2006] argued that the reduction of weathering in glaciated continental interiors would have been significant enough to negate the enhancing effect of exposed continental interiors.

The remainder of this paper consists of the following sections. Section 2 describes the climate model used in this study, and Section 3 describes the experimental setup. Results from transient (Section 4) and snapshot (Section 5) runs are then presented. Finally, concluding remarks are given in Section 6.

2 Model description

This study uses version 2.9 of the University of Victoria Earth System Climate Model (henceforth UVic ESCM, or UVic model), which is an intermediate complexity coupled atmosphere/ocean/sea-ice model with integrated land surface and vegetation schemes [*Weaver et al.*, 2001]. Its main component is version 2.2 of the GFDL Modular Ocean Model (MOM), a three-dimensional ocean general circulation model with 19 uneven vertical levels [*Pacanowski*, 1995], which is coupled to a vertically integrated energy-moisture balance atmosphere model [*Fanning and Weaver*, 1996], a dynamic-thermodynamic sea-ice model [*Bitz et al.*, 2001], a land surface scheme and dynamic global vegetation model [*Meissner et al.*, 2003], and a sedimentation model [*Archer*, 1996]. Land surface properties (surface temperature, soil moisture

content and temperature, and snow cover) and soil carbon content are computed with a single (1meter) layer version of the Meteorological Office Surface Exchange Scheme version 2 (MOSES-2) [*Cox et al.*, 1999], and terrestrial vegetation dynamics are handled by the Hadley Centre's Top-down Representation of Interactive Foliage and Flora Including Dynamics (TRIFFID) model [*Cox, 2001*]. TRIFFID describes the state of the terrestrial biosphere in terms of soil carbon content and vegetation distribution, which is expressed through the structure and coverage of five plant functional types: broadleaf tree, needleleaf tree, C₃ grass, C₄ grass, and shrub vegetation.

The UVic ESCM also includes a fully coupled global carbon cycle, which consists of inorganic carbon chemistry and land-surface exchanges of CO₂ [*Ewen et al.*, 2004], and a Nutrient-Phytoplankton-Zooplankton-Detritus (NPZD) module which calculates the contribution of the biological pump to ocean biogeochemistry [*Schartau and Oshlies*, 2003; *Schmittner et al.*, 2008]. Terrestrial carbon fluxes and reservoirs are described by *Matthews et al.* [2005], and coupled to the global model by *Meissner et al.* [2003].

The model is driven in the short term by seasonal variations in solar insolation and wind fields [*Kalnay et al.*, 1996], and in the long-term by orbital parameter changes and a reconstruction of atmospheric CO₂ content over the past 20 thousand years [*Indermühle et al.*, 1999]. The spatial coverage and height of continental ice sheets, which is prescribed every 1000 years using data from the model ICE-5G [*Peltier*, 2004], also acts as a driver of climate change during the deglacial period. The land-sea configuration used in all sub-components operates in a global spatial domain with a spherical grid resolution of 3.6° (zonal) by 1.8° (meridional), which is comparable to most coupled coarse-resolution AOGCMs. In the current configuration of the model, ocean bathymetry and sea level are static and fixed to present-day conditions, and thus some features of the LGM and deglacial period are not included here, such as the lower sea level and appearance of continental shelves in shallow portions of the current-day ocean.

Terrestrial weathering in the UVic model is parameterized as a land-to-ocean flux of dissolved inorganic carbon (F_{DIC}) and alkalinity (F_{ALK} , with $F_{ALK} = 2F_{DIC}$) via river discharge. In the standard version of the model, the incoming flux of carbon to the ocean as weathering is set to equal the sedimentation rate of CaCO₃ in order to balance the long-term carbon and alkalinity budgets in the ocean; the initial, steady-state value is typically held constant throughout the

transient model runs. This effectively suppresses the long-term negative feedback mechanism by preventing the weathering rate from adapting to changes in environmental factors such as temperature and atmospheric CO₂ concentration. *Meissner et al.* [2012] replaced the standard parameterization of weathering in the UVic model with a number of adaptations from previous carbon-cycle box models (see Section 3) in order to introduce and investigate the weathering negative feedback mechanism in the context of *future climate change scenarios*. They found that the long-term climate response to various emission scenarios depends almost exclusively on the total amount of CO₂ released, regardless of the rate at which it is being emitted, and that carbon uptake through an increase in terrestrial weathering has a significant effect on the climate system. There were, however, some differences between the various weathering schemes concerning the rate of carbon removal.

Using a similar approach as in *Meissner et al.* [2012], we introduced a set of box-model parameterizations of terrestrial weathering in order to examine potential impacts on the carbon cycle as weathering rates adjust to the increase in temperature and atmospheric CO_2 levels during *the latest deglacial period*. These weathering schemes were adapted from *Berner* [1994], *Lenton and Britton* [2006] and *Uchikawa and Zeebe* [2008], and a full description of their implementation into the UVic model is given by *Meissner et al.* [2012].

3 Methods

In this study we investigated the variation in rock weathering rate during the last deglacial period (16,000 - 4,000 BCE) using a box-model approach whereby we modulated the initial global weathering following changes to certain parameters: globally averaged surface air temperature (SAT), globally averaged atmospheric carbon dioxide concentration (CO₂), and globally summed vegetation net primary production (NPP). Our objective was to assess the potential impacts of deglacial climate change on the long term carbon cycle, notably through the changes in global chemical erosion rates and their effects on atmospheric carbon dioxide concentrations. To this end, various parameterizations of carbonate and silicate weathering were adapted to the UVic model in order to examine the scope of possible climate and carbon cycle responses. One model version called GEOCARB followed the parameterization introduced in GEOCARB II [*Berner*,

1994], which expresses the flux of weathering as a function of changes in temperature and atmospheric CO₂:

$$F_{Alk,w} = F_{Alk,w,0} \cdot g_{CO_2}(CO_2) \cdot [f_{Si} \cdot g_{Si}(SAT) + f_{Ca} \cdot g_{Ca}(SAT)]$$
(4)

$$F_{DIC,w} = F_{DIC,w,0} \cdot \left[f_{Si} + f_{Ca} \cdot g_{CO_2}(CO_2) \cdot g_{Ca}(SAT) \right]$$
(5)

where

$$g_{CO_2}(CO_2) = \left(\frac{2\frac{pCO_2}{pCO_{2,0}}}{1 + \frac{pCO_2}{pCO_{2,0}}}\right)^{0.4}$$
(6)

$$g_{Si}(SAT) = \left(1 + 0.038 \cdot (SAT - SAT_0)\right)^{0.65} \cdot e^{0.09 \cdot (SAT - SAT_0)}$$
(7)

 $g_{Ca}(SAT) = 1 + 0.087 \cdot (SAT - SAT_0)$ (8)

and $F_{Alk,w,0}$ and $F_{DIC,w,0}$ are the LGM riverine flux of alkalinity and dissolved inorganic carbon (DIC), pCO_2 is the atmospheric CO₂ concentration, *SAT* the global mean surface air temperature, and the index 0 denotes initial state (i.e., LGM) values. The factors f_{Si} and f_{Ca} stand for fraction of silicate (0.25) and carbonate (0,75) weathering, respectively [*Lenton and* Britton, 2006]; note that this fractionation is consistent with the knowledge at the time this model was created, and does not necessarily represent current views, which suggest a more evenly split [*Hartmann et al.*, 2009]. An adaptation of the GEOCARB models proposed by *Lenton and Britton* [2006], in which atmospheric CO₂ is replaced with the more variable vegetation net primary production rather than atmospheric CO₂, served as a second model version which we will refer to as LB:

$$F_{Alk,w} = F_{Alk,w,0} \cdot \left(\frac{NPP}{NPP_0}\right) \cdot \left[f_{Si} \cdot g_{Si}(SAT) + f_{Ca} \cdot g_{Ca}(SAT)\right]$$
(9)

$$F_{DIC,w} = F_{DIC,w,0} \cdot \left[f_{Si} + f_{Ca} \cdot \left(\frac{NPP}{NPP_0} \right) \cdot g_{Ca}(SAT) \right]$$
(10)

where *NPP* is the global mean net primary production. Our third version was based on an alternative formulation by *Uchikawa and Zeebe* [2008] and *Zeebe et al.* [2008], henceforth UZ, which loosely follows *Walker and Kasting* [1992] in calculating variations in global weathering intensity as a sole factor of atmospheric CO_2 content:

$$F_{Alk,w} = F_{Alk,w,0} \cdot \left[f_{Si} \cdot \left(\frac{pCO_2}{pCO_{2,0}} \right)^{0.6} + f_{Ca} \cdot \frac{pCO_2}{p_{CO}^2,0} \right]$$
(11)

$$F_{DIC,w} = F_{DIC,w,0} \cdot \left[f_{Si} + f_{Ca} \cdot \frac{pCO_2}{pCO_{2,0}} \right]$$
(12)

Finally, our fourth parameterization, called LGM, used fluxes of DIC and alkalinity which remained constant at their LGM value ($F_{Alk,w} = F_{Alk,w,0}$; $F_{DIC,w} = F_{DIC,w,0}$).

It is important to emphasize that these box-model parameterizations were taken out of their original, pre-industrial contextual frame, and applied to LGM and deglacial conditions. Initial temperature and NPP were calculated from a 10,000+ year equilibrium run with LGM (19,000 BCE) boundary conditions. LGM values for globally averaged temperature (9.15°C), globally summed NPP (39.3 Pg/yr), as well as weathering fluxes of DIC (0.12 Pg C/yr) and alkalinity (0.24 Pg C/yr), were in reasonable agreement with previous estimates of glacial conditions [Bluth and Kump, 1994; Brovkin et al., 2012]. The simulated glacial weathering DIC and alkalinity fluxes were somewhat lower than in other models; this discrepancy is mainly caused by the absence of LGM continental shelves in this version of the model, which causes it to underestimate the global rate of carbonate weathering. Variations in atmospheric CO₂ levels were prescribed based on ice core data from the Taylor Dome in Antarctica [Indermühle et al., 1999], and acted as the main driver of deglacial climate change alongside prescribed continental ice sheet retreat [*Peltier*, 1994] and astronomical changes in solar insolation [*Berger*, 1978]. Starting from LGM equilibrium values, the UVic model was integrated to year 4000BC (totaling 15,000 years) for each of the four weathering parameterizations described above. See section 4 for results.

The reasoning behind our prescribing of atmospheric CO_2 content lies in the inability of the UVic model to reproduce the observed trend of CO_2 during the deglacial period and early Holocene [*Simmons et al.*, 2016]. One of the major restrictions of this approach, however, is that it prevents assessing the direct response of atmospheric CO_2 content to changes in global weathering intensity, effectively limiting the investigation to changes in ocean biogeochemistry, notably the DIC and alkalinity content of the ocean. Hence, we devised a second set of experiments whereby fixed DIC and alkalinity weathering fluxes would be used to estimate potential changes in atmospheric CO_2 within long-term equilibrium run under appropriate

boundary conditions (ice sheet distribution, orbital parameters). The model was first spun up with 10,000 BCE and 15,000 BCE conditions and LGM (aka. 19,000 BCE) weathering fluxes. Then, for each respective time period, the values of those fluxes were increased by predetermined amounts (see Table 1), and the model was integrated for several thousand years for each set of DIC flux and alkalinity flux values. A total of 12 simulations were integrated and compared (see Table 1). This set of experiments, described in greater detail in Section 5, allowed us to explore the sensitivity of the atmospheric CO_2 response to the respective changes in weathering DIC and alkalinity fluxes, as well as the changes in this sensitivity through different stages of the deglacial period.

4 **Results – Ocean biogeochemistry (transient runs)**

The time series of atmospheric CO_2 concentration and simulated surface air temperature are shown in Figure 1, and their impact on global riverine DIC and alkalinity fluxes as calculated using the various weathering schemes are presented in Figure 2. Close similarities between the CO_2 curve in Figure 1 and the time series for the GEOCARB (red) and UZ (blue) parameterizations in Figure 2 support the idea that atmospheric CO_2 concentration is the primary driver of changes in global weathering intensity. Temperature was also factored into the GEOCARB parameterization, but it makes little difference here as globally averaged SAT change in the UVic model is mostly driven by changes in the CO_2 content of the atmosphere. It is noteworthy that the GEOCARB and UZ parameterizations produce similar results despite being derived from entirely independent empirical methods, both yielding a 15,000 year increase in DIC flux of about 0.03-0.04 Pg C/yr compared to the LGM control run (black).

Figure 2 also shows a considerable deviation of the LB (green) parameterization from GEOCARB and UZ. The almost twofold increase in DIC and alkalinity weathering fluxes by year 4000 BCE compared with the other model simulations is likely a consequence of LB accounting for changes in vegetation production, which increases drastically as northern vegetation expands into the previously ice-covered areas (see Figure 3b). It is interesting that no such deviation appeared in present-day simulations despite a much greater carbon cycle disruption (see UVic_LB curves in *Meissner et al.* [2012]). Although this can be partially explained by more significant variations in vegetation cover through the deglacial period, this

outcome is suggestive of the role of vegetation dynamics as a major driver of the weathering negative feedback mechanism during the period.

These differences notwithstanding, all (non-control) model versions used in the present study yield an observable increase in rock weathering rates, as evidenced by the rising fluxes of riverine DIC and alkalinity, along with the associated increases in ocean carbon content and alkalinity (Figure 4). The additional ocean DIC (~500 Pg C for GEOCARB and UZ, ~1000 Pg C for LB) represents only a small fraction of the total ocean carbon content of 37,500 Pg C, but it is not negligible nonetheless (especially when compared to the total change in atmospheric carbon content of 80 ppm, or 170 Pg C). Not surprisingly, the LB parameterization produces the highest amount of increase in ocean carbon content. More interestingly, we notice from Figure 2 that UZ produces slightly more DIC than GEOCARB, but less alkalinity. Despite this difference, the change in ocean carbon in Figure 4 suggests that GEOCARB weathering outputs slightly more DIC in the ocean, underlining the crucial role of alkalinity within the oceanic carbon cycle. The LGM parameterization, which represents the amount added to the ocean by the model without dynamic weathering changes, adds the least amount of carbon out of the four weathering schemes. For the latter case, the added carbon to the ocean results almost entirely from the prescribed increase in atmospheric CO₂, although all our simulations show an increase in ocean carbon in response to the increase in atmospheric CO₂ concentrations.

The time series of ocean alkalinity in Figure 4 presents a similar narrative, but with somewhat different metrics. Whereas LB weathering supplies more or less twice as much DIC to the ocean as the LGM parameterization, it increases ocean alkalinity by as much as eight times over that seen in the control run. Compared to the GEOCARB and UZ parameterizations, LB weathering sends approximately 1.5 times more DIC to the ocean, as opposed to an almost twofold increase in ocean alkalinity. This prominent increment in ocean alkalinity is indicative of an increase in global silicate weathering, which suggests at least some removal of CO_2 from the atmosphere.

The numbers obtained within the context of this study are subject to some important caveats, as the box model approach is missing some key elements of the deglacial period (notably, sea level changes, differences in the spatial configuration of rock types, and weathering under ice sheets) which can only be represented with a spatially explicit scheme. Our results are nonetheless consistent with the general box-model narrative that global weathering intensity should increase with global temperature and expanded vegetation cover, and can therefore be interpreted as a quantitative assessment of the strength of the weathering negative feedback mechanism during the deglacial period.

Of all the factors examined in this study, the parameterization of biological activity as either a function of CO₂ or NPP appears to be the most significant source of uncertainty between the model versions. This is characterized by the large difference between the output of LB and that of GEOCARB and UZ, which points to a much more significant impact of vegetation on weathering intensity when it is represented through changes in global production. Based on these results alone, it is difficult to assess whether the LB parameterization is an accurate representation of the biological enhancement of weathering or an overestimation. It could be argued that TRIFFID's consideration of climate and biochemical factors in its calculation of plant photosynthesis and respiration (which is reflected in NPP) is more sophisticated than the Michaelis-Menten function in GEOCARB (see equation 6). The latter is a fairly crude attempt to capture the CO₂ fertilization of weathering rate, which neglects the direct impacts of other important drivers and controls on plant productivity such as temperature and hydrology. The difference between the results of the simplistic GEOCARB function and the perhaps superior representation in LB suggests that vegetation dynamics is a very important control on global weathering rates and on the strength of the negative feedback mechanism; it is therefore important to further assess the effect of biogeophysical changes on weathering rates in future work, so as to reduce the key uncertainty in contributions to weathering changes during the last deglacial period.

5 Results – Changes in atmospheric CO₂ (equilibrium runs)

The experiments described in the previous section demonstrate the potential for deglacial weathering changes to affect the ocean carbon pool in a significant manner. From these prescribed CO_2 experiments, however, we are not able to show the effect this may have had on atmospheric CO_2 concentrations over this period. In this section, we therefore show a series of sensitivity simulations in which we allowed atmospheric CO_2 to freely evolve in response to different weathering rates at two different time periods during the deglacial period. Table 1 lists the combination of weathering DIC/alkalinity flux increases and paleo year (from which the

external forcings are determined – see Section 3) for each of the sensitivity tests. For the base experiments 10KY and 15KY, the increases in both DIC and alkalinity fluxes are approximately equal to the average increases produced by GEOCARB, UZ, and LB (see Section 4) at 10,000 BCE and 15,000 BCE, respectively. The notation "ALK" is appended to indicate that only the alkalinity flux has been increased for this experiment, likewise for "DIC" and the DIC flux. Finally, the "+" and "-" symbols denote cases where the increases in alkalinity and/or DIC fluxes do not correspond with the experiment's paleo year: a "+" ("-") sign indicates that weathering fluxes correspond to the averaged output of GEOCARB, UZ, and LB for a point in time 5,000 years later (earlier) than the paleo year. Note that we did not carry out a 15KY_DIC- or 15KY_ALK- simulation, as in this case there would not be any increase in weathering fluxes to drive changes in atmospheric CO₂ concentrations.

The time series of atmospheric CO_2 for the base experiments 10KY and 15KY, shown in Figure 5, suggest that the weathering negative feedback mechanism would have operated against the increasing CO_2 trend during the deglacial period and early Holocene. We obtain a reduction in atmospheric CO_2 concentration on the order of 16.5 ppm over 8000 years as a result of increasing weathering alkalinity and DIC fluxes from LGM to 10,000 BCE values, with everything else remaining equal. Integrating the model using 15,000 BCE weathering yields an atmospheric CO_2 decrease of 6.9 ppm, less than half as much as from 10KY. This difference can be mostly attributed to the lower alkalinity and DIC fluxes, rather than from the time period (see below).

The slow response time of atmospheric CO_2 arises from the long response timescale of ocean biogeochemistry to weathering inputs. It should be noted that ocean alkalinity and DIC are not in a quasi-equilibrium state after 8000 years, which implies that longer integration times would produce larger values of atmospheric CO_2 reduction. It can be argued however that any such values would have limited meaning given the timing of other perturbations to the carbon cycle from human activities associated with the beginning of the Anthropocene. We can therefore conclude from our 10,000 BCE equilibrium run that increases in alkalinity and DIC fluxes of 0.095 Pg C/yr and 0.035 Pg C/yr, respectively, would have by themselves produced a decrease in atmospheric CO_2 concentration of approximately 16.5 ppm over 8000 years, in opposition to the observed trend of increasing CO_2 concentrations.

The sensitivity tests presented here also outline the fundamental difference between alkalinity and DIC fluxes regarding their impact on the oceanic buffer factor (aka. $[HCO_3]$), which regulates air-sea exchanges of CO₂. To quantify this effect, we carried out a multivariate linear regression analysis based on the 8000-year difference in atmospheric CO₂ concentration for each of the alkalinity flux, and DIC flux combinations examined in this study; the resulting contour plot (Figure 6) illustrates the individual contributions of alkalinity and DIC fluxes to changes in atmospheric CO_2 content. The shape of Figure 6 suggests a relative independence of the two factors regarding their combined impact on atmospheric CO₂. Using a simplified factor separation analysis [Yin and Berger, 2012] with 10KY as f_{11} , 10KY_ALK as f_{10} , 10KY_DIC as f_{01} , and the initial condition as f_{00} , we find that the synergy between the two factors (aka. $\widehat{f_{11}}$) produces an additional decrease in atmospheric CO₂ of 5.5 ppm, which is much lower than the individual contributions of alkalinity (-33.9 ppm) and DIC (+22.9 ppm). In order to assess the importance of the paleo year (i.e., the external forcings), we can also compare 10KY_ALK (-33.9 ppm) with 15KY_ALK+ (-29.0 ppm), and 10KY_DIC (+22.9 ppm) with 15KYB_DIC+ (+13.8 ppm). There appears to be a greater impact on DIC flux than on alkalinity flux, perhaps due to differing ocean biogeochemistry between 10,000 BCE and 15,000 BCE initial conditions, but overall the effect of external forcings is considerably smaller than the change in weathering intensity. A similar outcome can be obtained by comparing the pairs of 15KY_ALK (-12.8 ppm) with 10KY_ALK- (-10.9 ppm), and 15KY_DIC (+4.3 ppm) with 10KY_DIC- (+9.5 ppm).

The main distinction between carbonate weathering and silicate weathering in the parameterizations used here lies in the fact that DIC fluxes to the ocean are only affected by carbonate weathering, whereas alkalinity increases as a result of both silicate and carbonate weathering. Based on our results (see Figure 6), it would then follow that the ratio of carbonate weathering to silicate weathering is a key determinant of the strength of the weathering feedback mechanism. In this study we used a global ratio of 25% silicate weathering to 75% carbonate weathering, as in *Meissner et al.* [2012]. Two-dimensional reconstructions of rock lithology in the literature suggest that the percentage of carbonate weathering could have ranged between 62% and 67% [*Meybeck et al.*, 1987; *Amiotte Suchet and Probst*, 1995; *Gaillardet et al.*, 1999] during modern times, and may have been as low as 57% during the LGM [*Ludwig et al.*, 1999; *Munhoven*, 2002], or perhaps even 50% [*Hartmann et al.*, 2009]. The slightly higher fraction of carbonate weathering used here may have resulted in a small underestimation of the impact of

weathering changes. Furthermore, since rock lithology (which determines the Ca/Si weathering ratio) is not uniformly distributed across the earth surface, it is possible that changes in the latitudinal distribution of weathering intensity – such as occurred during the latest deglacial period – would have had a profound impact on global weathering intensity.

6 Conclusions

In this paper, we examined the effect of deglacial weathering changes on ocean biogeochemistry and atmospheric CO_2 using a set of box model parameterizations of weathering fluxes within the UVic ESCM. We used weathering parameterizations based on temperature [Berner, 1994], atmospheric CO2 concentrations [Walker and Kasting, 1992; Uchikawa and Zeebe, 2008] and vegetation production [Lenton and Britton, 2006], first adapted to the model by Meissner et al. [2012], to diagnose the change in riverine alkalinity and DIC fluxes during the latest deglacial. The model was run from the end of the LGM (16,000 BCE) to the mid-Holocene (4,000 BCE) using prescribed changes in atmospheric CO₂, ice sheet configuration, and orbital parameters to drive climate change. Our results suggest that alkalinity and DIC fluxes may have increased by as little as 0.063 Pg C/yr and 0.024 Pg C/yr, respectively, or as much as 0.126 Pg C/yr and 0.044 Pg C/yr, respectively, between the LGM and the mid-Holocene. The expansion of vegetation following the retreat of continental ice and the resulting rapid increase in vegetation production are the main reasons for the differences in the results among the weathering parameterizations, and result from a very different treatment of biological enhancement of weathering by the various model versions. This indicates the importance of obtaining a better understanding of the effect of deglacial vegetation dynamic on the rock cycle.

We then prescribed the increases in alkalinity and DIC fluxes obtained from the transient model simulations into the model at specified time points (10,000 BCE and 15,000 BCE) in order to estimate the effect of these weathering changes on atmospheric CO_2 levels, and to separate the individual contributions of alkalinity and DIC, as well as the other external forcings (ice sheet distribution and orbital parameters). We found the impact on atmospheric CO_2 of changes in global weathering fluxes after 8000 model years to be on the order of a 16.5 ppm decrease for 10,000 BCE weathering levels, and about half as much for 15,000 BCE. The individual contributions of alkalinity and DIC were substantial and of opposite direction; where DIC inputs

alone led to a net loss of carbon from the ocean to the atmosphere, alkalinity inputs by themselves stimulated a significant CO_2 uptake into the ocean. These two effects combined relatively linearly, resulting in a net increase in ocean carbon (and associated drawdown of atmospheric CO_2) from increased weathering. Based on the different effects of carbonate and silicate weathering on alkalinity and DIC fluxes, these results suggest that the spatial distribution of rock lithology influences the strength of the weathering negative feedback mechanism. This becomes especially important when investigating the effects of land configuration changes, such as would have happened during the deglacial period. Although there are some examples in the literature of rock type driven, spatially-explicit weathering schemes [*Taylor et al.*, 2015; *Goddéris et al.*, 2006], none of these models are incorporated within intermediate complexity models and thus would be ill-suited to examine changes in weathering on glacial time scales. A two-dimensional weathering model taking into account the worldwide distribution of rock lithology, such as can be found in a recent version of the intermediate-complexity model GENIE [*Colbourn et al.*, 2013], would be better suited for further research in this direction.

This work has demonstrated that global rock weathering rates can be altered in a meaningful way during a period of large climate change such as the latest deglacial period, and can result in a nontrivial impact on the global carbon cycle. This box-model study does not take into account the subtleties of two-dimensional rock lithology distribution nor the important geographical changes in weathering distributions inherent to the deglacial period, as would have been induced from ice sheet retreat and sea level change. These are therefore important processes to include in further analyses of the effect of deglacial weathering changes on ocean biogeochemistry and climate change.

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Experiment name	Alkalinity difference*,1	DIC difference ^{*,2}	$\Delta \mathrm{CO}_2^{**}$
10KY	0.095	0.035	-16.5
10KY_ALK	0.095		-33.9
10KY_ALK+	0.142		-50.2
10KY_ALK-	0.035		-10.9
10KY_DIC		0.035	+22.9
10KY_DIC+		0.050	+32.8
10KY_DIC-		0.013	+9.5
15KY	0.035	0.013	-6.9
15KY_ALK	0.035		-12.8
15KY_ALK+	0.095		-29.0
15KY_DIC		0.013	+4.3
15KY_DIC+		0.035	+13.8

*All fluxes are given in units of Pg C/yr, and represent an increase from LGM values.

¹LGM value for weathering alkalinity flux is 0.24 Pg C/yr

²LGM value for weathering DIC flux is 0.12 Pg C/yr

** Change in atmospheric CO₂ concentration (ppm) after 8000 years of model integration.

Table 1. Increase in weathering DIC and alkalinity compared to LGM (19,000 BCE) values for each sensitivity test. Paleo year is indicated in the name of each experiment: 10,000 BCE if starting with 10KY, and 15,000 BCE if starting with 15KY. Paleo year determines the ice sheet configuration and orbital parameters used for each experiment. See Section 3 for further explanation of the notation.



Figure 1. Time series of observed atmospheric carbon dioxide concentration (top) and simulated surface air temperature (bottom). The data shown here are taken from the LGM model run, but it should be noted that the numbers are the same for each of the weathering schemes. More specifically, atmospheric CO_2 in this experiment is prescribed based on ice core data [*Indermühle et al.*, 1999] and is therefore not a model variable.



Figure 2. Difference time series of the global riverine flux of dissolved inorganic carbon (top) and alkalinity (bottom) into the ocean compared to the LGM (19,000 BCE) flux, for the weathering parameterizations GEOCARB (red), LB (green), UZ (blue), and LGM (black). The initial weathering fluxes of carbon and alkalinity is approximately 0.12 Pg C/yr and 0.24 Pg C/yr, respectively. The DIC and alkalinity values for 15KYBP, 10KYBP and 5KYBP used in Section 5 are also indicated. The values from "5KYBP" are used only in the 10KYBP_DIC+ and 10KYBP_ALK+ simulations.



total global vegetation carbon difference 19,000 BCE to 4000 BCE



Figure 3. Output of the vegetation model, shown here as (a) a time series of vegetation net primary production (top) and total carbon (bottom); and (b) a spatial distribution of vegetation carbon changes between years 16,000 BCE and 4,000 BCE. This plot represents the vegetation change as calculated from the LGM parameterization, but the output is similar for each of the weathering schemes. In panel (b) the extent of continental ice during the LGM is outlined in red.



Figure 4. Difference time series of the global oceanic carbon (top) and alkalinity (bottom) content, as compared with the LGM (19,000 BCE) values; results are compared for each of the weathering parameterizations GEOCARB (red), LB (green), UZ (blue), and LGM (black). The initial ocean carbon content and alkalinity are approximately 37,500 Pg C and 2.424 mol C/m³, respectively.



Figure 5. Difference time series of atmospheric CO_2 for experiments 10KY (solid) and 15KY (dotted), relative to the initial atmospheric concentrations of 251 ppm and 210 ppm, respectively.



Atmospheric CO₂ change according to increases in alkalinity and DIC fluxes

Figure 6. Contour plot of the 8000-year atmospheric CO_2 difference produced by any given combination of alkalinity flux difference (X axis) and DIC flux difference (Y axis), regressed from the results of several equilibrium runs. The experiments used to calculate the best fit are identified by black squares on the plot, and the adjacent label refers to the experiment's name in Table 1.

Chapter 4

The importance of terrestrial weathering changes in multimillennial recovery of the global carbon cycle: a two-dimensional perspective

The previous chapter has exposed the limitations of using box-model parameterizations to constrain global weathering intensity. The GEM-CO₂ model [*Amiotte Suchet et al.*, 1995] has incorporated a spatially-explicit weathering scheme by taking into account the heterogeneous distribution of lithologies across the world, and *Colbourn et al.* [2013] have shown that this paradigm can be successfully employed as a basis for the development of a two-dimensional weathering scheme in an intermediate-complexity climate model.

A spatially-explicit weathering scheme inspired from *Colbourn et al.* [2013] is developed for use within the UVic model, the specifics of which are described in this chapter along with an application to future climate changes. Results from the two-dimensional model are compared with model output using box-model parameterizations of weathering, as well as with results from other studies of future climatic changes and their impact on global weathering intensity. This chapter is based on a paper by authors Brault, M.-O., Matthews, H.D. and Mysak, L.A., which is submitted to the journal Earth System Dynamics.

The importance of terrestrial weathering changes in multimillennial recovery of the global carbon cycle: a two-dimensional perspective

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**Corresponding Author*: Marc-Olivier Brault, Department of Geography, McGill University Montreal, Canada H3A 0B9. E-mail: marc-olivier.brault@mail.mcgill.ca In this paper, we describe the development and application of a new spatially-explicit weathering scheme within the University of Victoria Earth System Climate Model (UVic ESCM). We integrated a dataset of modern-day lithology with a number of previously devised parameterizations for weathering dependency on temperature, primary productivity, and runoff. We tested the model with simulations of future carbon cycle perturbations, comparing a number of emission scenarios and model versions with each other and with zero-dimensional equivalents of each experiment. Overall, we found that our two-dimensional weathering model versions were more efficient in restoring the carbon cycle to its pre-industrial state following the pulse emissions than their zero-dimensional counterparts; however, in either case the effect of this weathering negative feedback on the global carbon cycle was small on timescales of less than 1000 years. According to model results, the largest contribution to future changes in weathering rates came from the expansion of tropical and mid-latitude vegetation in grid cells dominated by weathering-vulnerable rock types, whereas changes in temperature and river runoff had a more modest direct effect. Our results also confirmed that silicate weathering is the only mechanism that can lead to a full recovery of the carbon cycle to pre-industrial levels on multi-millennial timescales.

1 Introduction

1.1 Rationale

The weathering of carbonate and silicate rocks on land is a key process in the global carbon cycle and, through its coupling with calcium carbonate deposition in the ocean, is the primary sink of carbon on geologic timescales [*Urey*, 1952; *Walker et al.*, 1981]. The rate at which these processes remove carbon from the Earth system is sensitive to changes in the environment, notably temperature [*Berner*, 1991], biological productivity [*Lenton and Britton*, 2006] and perhaps more indirectly, river runoff [*Walker and Kasting*, 1992]. This gives rise to a negative feedback mechanism which regulates the global climate on multimillennial time scales. However, there have been but very few quantitative assessments of its impacts on carbon cycling and ocean biogeochemistry, and its relevance over time frames of 10^4 years or shorter is largely unknown.

Here, we introduce a new model of rock weathering developed for use within the University of Victoria Earth System Climate Model (UVic ESCM); this model incorporates a spatially explicit interactive computation of weathering rates to close the global carbon cycle on multi-millennial time scales. The model is based on a lithology-dependent calculation of steady-state weathering fluxes, which are modulated by transient changes in environmental conditions akin to the 0-D carbon cycle models already present in the literature [e.g. *Meissner et al.*, 2012]. We tested the model with simulations of future climate changes following anthropogenic carbon emissions, comparing the output to that of earlier weathering models, both 2-D [*Colbourn et al.*, 2013] and 0-D [*Lenton and Britton*, 2006].

1.2 The rock weathering cycle

The chemical weathering of rocks is characterized by the cleavage of bonds of the mineral lattice by water, often in the presence of a secondary weathering agent – hydronium or OH ions, low molecular weight organic chelators, or carbonic acid (H_2CO_3 ; a product of carbon dioxide dissolution in rainwater). Rock weathering products, including calcium and bicarbonate ions (respectively the most abundant cation and anion in most river waters), can be carried away with runoff to rivers and into the ocean. For example, calcium carbonate dissolution by carbonic acid is given by [*Archer et al.*, 1997]:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$
 (1)

The influx of dissolved inorganic carbon (henceforth DIC) and alkalinity to the ocean surface layer is balanced by the precipitation and burial of biogenic calcium carbonate (CaCO₃) in the marine sediments, and ocean alkalinity is a key factor in determining the carbonate compensation depth (CCD), the depth below which the dissolution rate of calcium carbonate exceeds its precipitation rate. In the long term this allows the ocean to maintain a remarkably stable alkalinity, as any increases in ocean acidity (such as can be caused by a CO₂ invasion from the atmosphere) can be neutralized by elevating the CCD, which dissolves carbonate sediments and releases carbonate ions (CO₃²⁻) back into the ocean. This oceanic buffer factor, along with carbonate dissolution on land (due to weathering), is the primary means through which ocean alkalinity is restored, and is responsible for maintaining both atmospheric and oceanic pCO₂ close to equilibrium. In short, the weathering of calcium carbonate can accelerate the transfer of CO₂ between the atmosphere and ocean, but does not contribute to a permanent return of carbon to the geologic reservoir [*Ridgwell and Zeebe*, 2005; *Sarmiento and Gruber*, 2006].

A certain fraction of rock weathering reactions involve a weakening of chemical bonds in the mineral lattice on contact with water whereby hydrogen ions replace positively charged cations (mostly Ca^{2+} and Mg^{2+}) which are bounded to negatively charged ions, most particularly SiO₄ (silicate) structures. One of the most common examples is given by calcium silicate hydrolysis, as described by following schematic reaction [*Ebelmen*, 1845; *Urey*, 1952]:

$$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + H_4SiO_4 + 2HCO_3^-$$
 (2)

This equation represents the weathering of any silicate mineral into silicic acid (which often precipitates as amorphous silica SiO_2), and consumes one more molecule of CO_2 than carbonate dissolution while sending the same amounts of calcium and bicarbonate ions to the ocean. The combination of equation (2) with calcium carbonate precipitation (the reverse of equation 1) shows how this results in a net removal of one molecule of CO_2 :

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$
(3)

Weathering rates due to silicate hydrolysis tend to be considerably slower than from the dissolution of carbonate minerals – it removes on average 0.28 to 0.30 Pg C per year [Amiotte

Suchet and Probst, 1995] – hence the effect of atmospheric CO_2 consumption by silicate weathering only becomes a significant sink of carbon on geologic timescales (10^5-10^6+ years). For the remainder of this article, dissolution of carbonates (on land) and hydrolysis of silicates will be treated separately and referred to as carbonate and silicate weathering, respectively.

1.3 Weathering in early carbon cycle models

Variations in rock weathering rates have long been believed to hold a major role in regulating the Earth's long-term climate, and early (non-spatially explicit) carbon cycle models were built to investigate the importance of the weathering feedback mechanism on various events in Earth's geological history. *Walker, Hays and Kasting* [1981], henceforth referred to as WHAK, developed expressions relating silicate weathering rates to atmospheric pCO_2 (indirectly through vegetation productivity) and temperature (including a weak dependency on runoff) and used them to offer a solution to the faint young Sun paradox by providing a convenient mechanism for a slow and steady decrease in atmospheric greenhouse gas concentrations. *Berner, Lasaga and Garrels* [1983], henceforth referred to as BLAG, also linked the rate of atmospheric CO₂ consumption by silicate weathering to changes in surface air temperature, atmospheric partial CO₂ pressure, and river runoff and offered this dependency as a possible explanation for the general decreasing trend of atmospheric CO₂ levels on geologic timescales. Although these models used rudimentary parameterizations derived from early general circulation models and experimental data, they built a foundation for future long-term carbon cycle model studies.

Following BLAG, *Berner* [1991] built a geochemical cycle model in which the long-term evolution of atmospheric carbon content would be driven by imbalances between CO_2 outgassing by volcanic activity and the burial of carbonate sediments following the weathering of silicate rocks. The latter was given a dependency on air temperature and atmospheric CO_2 , and it was used to solve a series of mass balance equations in order to determine the inward and outward fluxes for the atmosphere-ocean, land, and mineralogical carbon reservoirs. This new model, called GEOCARB, added more direct biological mechanisms (notably, the soil-biological enhancement of weathering) and introduced land elevation and runoff as independent parameters. Much like its predecessor, this model was developed in order to reconstruct the evolution of atmospheric pCO_2 over the past hundreds of millions of years. Subsequent versions were called GEOCARB II [*Berner*, 1994] and GEOCARB III [*Berner and Kothavala*, 2001], and

these further improved the weathering parameterizations based on the latest observational data and GCM output. They were later coupled with a model of atmospheric O_2 and ocean nutrients to create COPSE [*Bergman et al.*, 2004], a multi-element geochemical cycling model which introduces a feedback-based interaction between biotic and abiotic elements of the Earth system.

1.4 Modelling the lifetime of anthropogenic CO₂

A number of studies have addressed the consequences of anthropogenic carbon emissions and the multi-millennial lifetime of its perturbation on the climate system. The earliest attempt to quantify the timescale of the weathering negative feedback mechanism can be traced back to *Sundquist* [1991], who used a coupled atmosphere-ocean-carbon cycle model to obtain an e-folding timescale on the order of several 10^5 years. Other studies have quantified this timescale with values of 200 kyr [*Archer et al.*, 1997] and 400 kyr [*Berner and Kothavala*, 2001; *Archer*, 2005] or more [*Colbourn et al.*, 2015]. Most recent work on this matter [*Ridgwell and Hargreaves*, 2007; *Montenegro et al.*, 2007; *Uchikawa and Zeebe*, 2008; *Archer et al.*, 2009; *Eby et al.*, 2009] has involved intermediate-complexity models, which are usually limited in scope to 10^4 years or shorter. Hence the weathering feedback mechanism in these studies is limited to the pH neutralization effect of carbonate weathering on the oceans (which restores the lysocline to its original depth), and silicate weathering is either ignored altogether or prescribed as a global constant average flux.

In a pioneering study, *Walker and Kasting* [1992] considered the impact of the rock cycle and carbonate sediment dissolution in projections of future changes in the global carbon cycle. Their model was built on the assumption that the dependency of carbonate and silicate weathering rates to changes in the carbon cycle (aka. atmospheric CO_2 levels) was purely abiotic, which was in line with the other geochemical cycling models of the time. Following on *Walker and Kasting* [1992] as well as the recent innovations in COPSE, *Lenton and Britton* [2006] posited that biological changes in the Earth system could further enhance the increase or decrease in rock weathering rates, especially in the context of a rapidly warming world which would likely result from unabated anthropogenic emissions. Their carbon cycle model included sophisticated biotic and abiotic transports of carbon, introducing a box-model representation of carbonate and silicate weathering processes in which weathering rates were directly dependent on plant productivity, rather than on atmospheric CO_2 concentrations. This allowed them to investigate the role of land

use changes on the long-term recovery of atmospheric CO_2 ; in particular, they found that vegetation-suppressing land use changes would force CO_2 levels to stabilize above preindustrial levels on geologic timescales, thus indefinitely trapping some of the anthropogenic emissions in the atmosphere.

1.5 On spatially-explicit weathering models

Few attempts have been made to explore the spatial variability of carbonate and silicate weathering rates and how it may affect the global efficacy of the weathering negative feedback mechanism. The main problematic relating to the development of spatially explicit weathering schemes is the necessity to compute weathering individually for each land grid cell, which is entirely more complex than using a globally-averaged value, for which many precedents exist in the literature. The GEM-CO₂ model [Amiotte Suchet and Probst, 1995] addressed this problem by defining the spatial variability in terms of rock types, and using data for bicarbonate (HCO₃) concentration and runoff collected over various mono-lithologic drainage basins [Meybeck, 1987] to establish empirical linear relationships between weathering flux and runoff for a series of major rock types. Arguing that these two factors (runoff and rock type) were the main factors controlling the consumption of atmospheric/soil CO₂ by weathering, they calculated the global distribution of CO₂ consumption. Their results showed a higher intensity of weathering in the Northern Hemisphere (due to rock type) and in equatorial regions (due to runoff). They later refined the global distribution of rock types by attributing one of six rock types to each land unit of a 1°×1° grid [Amiotte Suchet et al., 2003]; this distribution will be used as the basis for our spatially explicit weathering scheme. Rock types, from having the smallest to largest impact on weathering, are classified as follows: plutonic and metamorphic (shield) rocks, sands and sandstones, extrusive igneous (acid volcanic) rocks, basalts, shales and evaporites, and carbonate rocks. The latter designs a loose group of predominantly carbonate-based rocks, and of the other five rock types only sandstones and shales contain a fraction of carbonate-weathered minerals. In the other rock types, the prevalence of carbonate minerals is too variable and difficult to estimate, hence they are assumed to contain only silicate-weathered minerals. Using the GEM-CO₂ model, carbonate rocks and shales were found to both consume 40% of the total continental CO₂ uptake despite occupying a much smaller fraction of land area, while sandstones and shield rocks contributed much lower than their outcrop abundance. A similar rock type distribution
was developed [*Gibbs and Kump*, 1994; *Bluth and Kump*, 1994] (hence GKWM), using both an empirical linear coefficient and an exponential factor to express weathering dependence on runoff for different rock types; however the results produced by their lithological distribution was found to be very similar to that of GEM-CO₂, in terms of global weathering intensity and the consumption of atmospheric/soil CO₂ [*Colbourn et al.*, 2013].

Other instances of spatially-explicit weathering models are few in the literature. The GEOCLIM model has a built-in two-dimensional weathering scheme that has been used to investigate the climatic impacts of tectonic continental reorganization and weathering-vegetation interactions [*Donnadieu et al.*, 2009]. More recently, a spatially-explicit scheme was added to the GENIE model [*Colbourn et al.*, 2013], using lithological databases from the GEM-CO₂ and GKWM models, temperature dependency from the GEOCARB models, NPP dependency as introduced by *Lenton and Britton* [2006], and runoff dependency from GEM-CO₂. Although the paper focused mostly on exploring the various model options, the authors were able to simulate the entirety of the climate system recovery from a 5000 Pg C anthropogenic pulse at year 2000, showing that within 0.5-1 Myr the atmospheric CO₂ levels would return to pre-industrial levels.

2 Methods

2.1 Climate model description

In this study we used version 2.9 of the University of Victoria Earth System Climate Model (henceforth UVic ESCM, or Uvic model), which is an intermediate complexity coupled atmosphere/ocean/sea-ice model with integrated land surface and vegetation schemes [*Weaver et al.*, 2001]. Its main component is version 2.2 of the GFDL Modular Ocean Model (MOM), a three-dimensional ocean general circulation model with 19 uneven vertical levels [*Pacanowski*, 1995], which is coupled to a vertically integrated energy-moisture balance atmosphere model [*Fanning and Weaver*, 1996], a dynamic-thermodynamic sea-ice model [*Bitz et al.*, 2001], a land surface scheme and dynamic global vegetation model [*Meissner et al.*, 2003], and a sedimentation model [*Archer*, 1996]. Land surface properties (surface temperature, soil moisture content and temperature, and snow cover) and soil carbon content are computed with a single (1-meter) layer version of the Meteorological Office Surface Exchange Scheme version 2 (MOSES-

2) [*Cox et al.*, 1999], and terrestrial vegetation dynamics are handled by the Hadley Centre's Top-down Representation of Interactive Foliage and Flora Including Dynamics (TRIFFID) model [*Cox*, 2001]. TRIFFID describes the state of the terrestrial biosphere in terms of soil carbon content and vegetation distribution, which is expressed through the structure and coverage of five plant functional types: broadleaf tree, needleleaf tree, C_3 grass, C_4 grass, and shrub vegetation.

The UVic ESCM also includes a fully coupled global carbon cycle, which consists of inorganic carbon chemistry and land-surface exchanges of CO₂ [*Ewen et al.*, 2004], and a Nutrient-Phytoplankton-Zooplankton-Detritus (NPZD) module which calculates the contribution of the biological pump to ocean biogeochemistry [*Schartau and Oshlies*, 2003; *Schmittner et al.*, 2008]. Terrestrial carbon fluxes and reservoirs are described by *Matthews et al.* [2005], and coupled to the global model by *Meissner et al.* [2003].

The model is driven in the short term by seasonal variations in solar insolation and wind fields [*Kalnay et al.*, 1996], and in the long-term by orbital parameter changes and a reconstruction of atmospheric CO₂ content over the past 20 thousand years [*Indermühle et al.*, 1999]. The spatial coverage and height of continental ice sheets is prescribed every 1000 years using data from the model ICE-5G [*Peltier*, 2004]; thus these ice sheet configurations also serve to drive climate changes during glacial periods. The land-sea configuration used in all sub-components operates in a global spatial domain with a spherical grid resolution of 3.6° (zonal) by 1.8° (meridional), which is comparable to most coupled coarse-resolution AOGCMs.

2.2 Weathering model description

Terrestrial weathering in the UVic model is parameterized as a land-to-ocean flux of dissolved inorganic carbon (F_{DIC}) and alkalinity (F_{ALK} , with $F_{ALK} = 2F_{DIC}$) via river discharge. In the standard version of the model, the incoming flux of carbon to the ocean as weathering is set to equal the sedimentation rate of CaCO₃ in order to balance the long-term carbon and alkalinity budgets in the ocean; the initial, steady-state value is typically held constant throughout the transient model runs. This effectively suppresses the long-term negative feedback mechanism by preventing the weathering rate from adapting to changes in environmental factors such as temperature and atmospheric CO₂ concentration. *Meissner et al.* [2012] replaced the standard

parameterization of weathering in the UVic model with a number of adaptations from previous carbon-cycle box models in order to investigate the role of rock weathering as a carbon sink for anthropogenic carbon emissions. They found that the long-term climate response to various emission scenarios depends almost exclusively on the total amount of CO_2 released regardless of the rate at which it is being emitted, and carbon uptake through an increase in terrestrial weathering has a significant effect on the climate system. There were, however, some differences between the various weathering schemes concerning the rate of carbon removal.

In this section we describe a spatially explicit weathering scheme developed for use within the UVic ESCM. Steady-state carbonate and silicate weathering rates are calculated for each land grid cell based on the local rock type (Sect. 2.2.1) and runoff (Sect. 2.2.2). In transient model runs, these values are modulated by changes in temperature, atmospheric CO_2 concentrations or vegetation productivity, and runoff (Sect. 2.2.3), which are updated on each time step based on model output. Changes in carbonate and silicate weathering rates are returned to the model in the form of a riverine flux of carbon and alkalinity (Sect. 2.2.4), which is routed to the ocean.

2.2.1 Worldwide distribution of rock types

The two-dimensionality of the weathering model is rooted in the uneven distribution of rock types across the world. Thus, regions with more active lithologies (mostly sedimentary rocks such as carbonates and shales) yield higher weathering rates under similar climate conditions, and these are more sensitive to changes in climate controls than regions predominantly covered by weathering-resistant lithologies (igneous and metamorphic rocks, basalts and granites). Whereas the worldwide distribution of continental rock lithology is well known, there is only limited knowledge of the impact of different rock types on the amounts of riverine exports, therefore any estimation of weathering rates based on local lithological composition is subject to some discrepancy. Two of the most prominent spatially explicit weathering schemes, the Gibbs and Kump weathering model [*Gibbs and Kump*, 1994], and GEM-CO2 [*Amiotte Suchet and Probst*, 1995], each use their own set of land lithological data, which classify the entirety of the world's lithologies into one of several rock types, defining the impact of each on weathering by modifying its basic dependency on runoff. While developing a 2-D weathering model for use into the climate model GENIE, *Colbourn et al.* [2013] compared the output generated by both lithological distributions. They found that the end result did not differ much between the two

models (they found a difference of only 4 ppm in atmospheric CO_2 concentration 100 kyr following a pulse of 5000 Pg C in the atmosphere), concluding that differences between individual rock distribution datasets have a negligible impact on the model output.

In this study we used the lithological distribution paradigm first introduced in GEM-CO₂, and later published by *Amiotte Suchet et al.* [2003]. The flux of atmospheric/soil CO₂ from chemical weathering on each continental grid cell was given an empirical linear relationship to runoff (see Sec. 2.2.2) depending on its assigned predominant rock type, which was classified as one of six different lithological categories: sands and sandstones, shales, carbonate rocks, shield rocks, acid volcanic rocks, and basalts. Sedimentary rocks (limestones, shales, sandstones) contain significant amounts of carbonate rocks, and thus do not consume atmospheric CO₂ as efficiently as their weathering output would suggest.

The adaptation of the rock type distribution map to the UVic model is shown in Figure 1. The spatial resolution of the UVic model $(3.6^{\circ} \times 1.8^{\circ})$ is about 6.5 times coarser than that of the original database $(1^{\circ} \times 1^{\circ})$ hence the adapted rock distribution paradigm was defined according to the partitioning of rock types within the area contained by each UVic model grid cell. The resulting runoff multiplier and carbonate to silicate fractionation therefore becomes a weighted spatial average of all of rock type multipliers in Table 1.

2.2.2 Calculating the steady-state weathering rate

The reference weathering rate is calculated for each individual grid cell based on local steadystate runoff R_0 (Figure 2a) and rock type composition. Following *Amiotte Suchet and Probst* [1995], the local riverine fluxes of bicarbonate ions from carbonate (f_{Ca}) and silicate (f_{Si}) weathering are computed as:

$$f_{Ca} = R_0 \sum_{i} frac_i k_i \alpha_i \tag{5}$$

$$f_{Si} = R_0 \sum_{i} frac_i k_i (1 - \alpha_i) \tag{6}$$

where $frac_i$ is the fraction of rock type *i* present in the grid cell, k_i is the rock type specific weathering rate multiplier, and α_i is the fraction of rock type given to weather as carbonate rocks. The different rock types and their weathering parameters are shown in Table 1. The weathering rate multipliers (k_i) were derived from the data by *Amiotte Suchet et al.* [2003] and

the fractionation of rock types between carbonate and silicate rocks is adapted from the work of *Gibbs et al.* [1999], following the interpretation of *Colbourn et al.* [2013].

The resulting steady-state carbonate and silicate weathering rates at pre-industrial (1800AD) conditions are shown in Figure 2b. There is a noticeable concentration of CaCO₃ weathering in areas of high runoff with bedrock composed predominantly of carbonate rocks (for example, Southeast Asia), whereas $CaSiO_3$ weathering is spread more evenly across the world. It is noteworthy that the Amazon basin features by far the highest runoff yet produces unremarkable weathering rates (compared to other tropical areas) due to the prevalence of the weatheringresistant shield rocks. The same observation can be used to explain the low weathering rates in This weathering distribution compares reasonably well with the CO₂ central Africa. consumption distribution found by Amiotte Suchet and Probst [1995], but it doesn't reproduce the large values at northern high latitudes (especially in northern Asia) that can be found using the GEM-CO₂ model. The distribution of bicarbonate fluxes of Gibbs and Kump [1994] displays a somewhat lower equator-to-pole gradient in weathering rates, and suggests an area of high weathering in the southeast USA which is not reproduced with our model, mainly on account of low runoff in the region. These discrepancies are likely due to precipitation bias in the UVic ESCM. However, both models appear to agree with our finding that southeastern Asia is the region with the highest regional weathering intensity. Globally, the 2-D weathering scheme sends a DIC flux of 0.166 Pg C/y into the ocean, which is approximately 15% more than the 0-D model output (0.145 Pg C/yr) [Meissner et al., 2012], and on par with previous estimations of pre-industrial global weathering intensity.

2.2.3 Modulation of weathering rate

In transient model simulations, the carbonate and silicate weathering rate for each grid cell is modulated by changes in local environmental conditions. They were made dependent on surface air temperature, atmospheric carbon dioxide content, and runoff in a similar manner to previous carbon cycling models. Following *Lenton and Britton* [2006], we have included the option of replacing the dependency on CO_2 concentration by vegetation productivity, which more directly accounts for the impact of biological factors on weathering intensity.

Temperature is a known controller of weathering intensity as higher temperatures increase the kinetic energy of molecules, facilitating the atomic encounters which lead to the chemical

dissociation of minerals. Although it is impossible to derive a relationship between temperature and weathering rates from first principles, laboratory and field studies have correlated the concentration of bicarbonate ions in a solution to water temperature in order to develop an empirical formulation. For carbonate weathering, we used the results of *Harmon et al.* [1975], who compared the groundwater temperature and bicarbonate ion concentration of several North American watersheds to come up with the following empirical relationship:

$$g_{Ca}(SAT) = 1 + 0.049(SAT - SAT_0) \tag{7}$$

where SAT and SAT_0 are the transient and steady-state surface air temperature, respectively. For silicate weathering, we used a version of the Arrhenius rate law of *Brady* [1991] which was adapted into the RokGeM model by *Colbourn et al.* [2013]:

$$g_{Si}(SAT) = e^{0.09(SAT - SAT_0)}$$
(8)

Here, the constant of 0.09 inside the exponential expression was obtained using an activation energy of 63 kJ mol⁻¹ for silicate weathering and a global initial temperature of 288K (global average pre-industrial temperature). The activation energy is poorly constrained, but has been shown to have little effect on the long-term consumption of atmospheric CO_2 ; nevertheless, it is crucial to determining the strength of the feedback between climate and weathering.

The productivity dependence of weathering serves to illustrate the biological and soilenhancement factors which control weathering intensity, with vegetation net primary productivity a suitable proxy for biological activity in an area. *Lenton and Britton* [2006] introduced a simple linear dependence of weathering on productivity based on the steady-state proportion of global productivity to global weathering flux:

$$g(NPP) = \frac{NPP}{NPP_0} \tag{9}$$

where NPP and NPP_0 are the transient and steady state net primary production, respectively, taken explicitly from the output of the coupled land surface scheme MOSES-2 and vegetation module TRIFFID. This formulation works reasonably well in 0-D models with globally-summed values of productivity and weathering rate; however, some problems arise when trying to use it in a spatially-explicit model due to its inherent assumption that productivity and weathering intensity are directly related at steady state. A good example of this would be at the continental margins of predominantly ice-covered continental landmasses (Greenland,

Antarctica) where some of the land may be ice-free, but too cold to support any vegetation. However, the presence of nearby ice sheets generates a meltwater runoff flux which greatly enhances weathering, in spite of the lack of vegetation. Therefore, any expansion of vegetation in this area, however small (which is not unrealistic given the extreme warming scenarios examined here), would result in an unreasonable increase in weathering. In order to rectify this situation, we have introduced a modified version of equation 9 which calculates the increase in local weathering rate when *NPP* is greater than its steady-state value:

$$g(NPP) = \begin{cases} NPP/NPP_{0}, & NPP < NPP_{0} \\ \left(\frac{(NPP - NPP_{0})}{NPP_{0,global}} \right) \\ 1 + \frac{f_{0}}{f_{0,global}} \end{pmatrix}, & NPP \ge NPP_{0} \end{cases}$$
(10)

where $f_0 = f_{Ca} + f_{Si}$ and the "global" indices indicate the globally-summed value of that variable. The right-hand term in the brackets is a compensation term, which modifies the increase in weathering based on the relative contribution of the grid cell to the global productivity compared with its contribution to the global weathering flux. This results in a redistribution of NPP-induced changes in weathering without changing the globally-summed increase in weathering intensity (this is true only in the absence of other controlling factors, such as temperature). Note that the parameterization is unchanged from equation (9) whenever NPP is lower than its initial value, mostly to avoid computing negative values of g(NPP). This has a relatively benign impact on the global result, as the values calculated from equation (10) only differ significantly from those of equation (9) when NPP is much greater than NPP₀.

As an alternative to productivity dependence, we also included the option to parameterize weathering as a function of atmospheric CO_2 content, following the approach used in the GEOCARB II model of *Berner* [1994]:

$$g(CO_2) = \left(\frac{2\frac{pCO_2}{pCO_{2,0}}}{1 + \frac{pCO_2}{pCO_{2,0}}}\right)^{0.4}$$
(11)

where pCO_2 and $pCO_{2,0}$ are the transient and steady-state atmospheric concentration of CO₂, respectively. This relationship has long been used to estimate the fertilizing effect of CO₂ on

land plants, and thus becomes here an indirect parameterization of the biological enhancement of weathering. It can be used *in lieu* of equations 9 and 10 as a model option. Note that many recent model versions, including GEOCARB III, reject the exponent of 0.4 on grounds that most plants do not in fact respond to CO_2 fertilization.

Runoff is the most widely used factor of weathering intensity as it constitutes a good proxy for the strength of the water cycle in an area. One may consider the fact that high runoff environments tend to be associated with intense weather activity (the rainforests, for example), and also that stagnant waters quickly become saturated, thus limiting the efficiency of weathering. Given that we already include runoff in the calculation of steady-state weathering, the transient runoff dependency is a simple adjustment following *Berner* [1994]:

$$g_{Ca}(R) = \frac{R}{R_0} \tag{12}$$

$$g_{Si}(R) = \left(\frac{R}{R_0}\right)^{0.65} \tag{13}$$

where R and R_0 are the transient and steady-state river runoff, respectively, which are also taken explicitly from the output of the land surface scheme MOSES-2. The difference between the formulations for carbonate and silicate weathering is an empirical correction based on the assumption that bicarbonates from the weathering of silicate rocks are more diluted in rivers than for carbonate weathering. The value of 0.65 in equation (13) was taken from *Berner* [1994]; although the value itself has a large margin of error, it has been shown to have only a modest effect on the overall efficiency of the weathering feedback mechanism.

To summarize, we have developed a two-dimensional weathering scheme whereby the steadystate values of carbonate and silicate weathering fluxes (see Sect. 2.2.2) are modulated by changes in temperature, vegetation productivity (alternatively: atmospheric CO2 concentration), and runoff. Thus the complete weathering parameterizations take the form:

$$F_{Ca} = f_{Ca} \cdot g_{Ca}(SAT) \cdot g(NPP) \cdot g_{Ca}(R)$$
(14)

$$F_{Si} = f_{Si} \cdot g_{Si}(SAT) \cdot g(NPP) \cdot g_{Si}(R)$$
(15)

Weathering is calculated in each individual land grid cell, and routed to the coastal ocean as fluxes of alkalinity and dissolved inorganic carbon, explained in section 2.2.4.

2.2.4 Effects of weathering on ocean biogeochemistry

In the UVic ESCM, weathering does not have a direct impact on atmospheric or land surface carbon; its effects are prescribed through the riverine exports of weathering products which are sent to the ocean and modify its chemical composition. The chemical weathering processes are described by equations 1 (carbonate) and 2 (silicate), both resulting in a flux of two moles of bicarbonate ions (HCO₃⁻). The flux of dissolved inorganic carbon (F_{DIC}) is counterbalanced by the consumption of atmospheric carbon dioxide during the weathering reactions, leaving a net DIC flux of one mole for carbonate weathering, and none for silicate weathering; a constant term was also added to represent the contribution of volcanic outgassing to global carbon emissions (which is not included in the UVic model):

$$F_{DIC} = F_{Ca} + F_{volc} \tag{16}$$

Given that, in the absence of external forcings, the CO₂ consumption by silicate weathering is meant to counter the intake of carbon from the geologic reservoir from volcanic eruptions, we set the constant term F_{volc} to equal the steady-state flux of silicate weathering ($F_{volc} = F_{Si,0}$). Meanwhile, the net flux of alkalinity (F_{ALK}) remains equal to the flux of bicarbonate ions. The above discussion is summarized in the following set of equations, which describes the partitioning of carbonate weathering and silicate weathering fluxes into dissolved inorganic carbon and alkalinity fluxes, which are then globally summed and fed to the ocean biogeochemistry module:

$$F_{DIC} = F_{Ca} + F_{Si,0} \tag{17}$$

$$F_{ALK} = 2F_{Ca} + 2F_{Si} \tag{18}$$

Note that our choice of F_{volc} effectively equilibrates ocean biogeochemistry during equilibrium runs ($F_{ALK,0} = 2F_{DIC,0}$). The values calculated here represent net fluxes over the entire surficial (atmosphere-land-ocean) reservoir, and in particular the simplification for the net flux of DIC is based on the assumption that the consumption of CO₂ from the atmosphere is immediately balanced by an equivalent uptake of carbon from the ocean. This would be true in general, given that the timescale of the weathering negative feedback mechanism far exceeds that of atmosphere-ocean mixing; however in the timescales considered here (10^3 - 10^4 yr) there would be some delay between the consumption of CO₂ from the atmosphere and the release of CO₂ in the ocean following CaCO₃ burial. This delay would not significantly alter the impact of weathering

on atmospheric geochemistry, but could reduce by as much as 10% the rate at which alkalinity increases in the ocean [*Colbourn et al.*, 2013].

2.3 Steady-state weathering and description of transient model simulations

Pre-industrial steady-state weathering was obtained by integrating the model for over 20,000 years under year 1800 boundary conditions, using rock type dependency and distribution as detailed in sections 3.1.1 and 3.1.2. Land-to-ocean weathering fluxes stabilized in less than 10^3 years, on account of runoff being mostly computed from atmospheric output. However, the fixing of deep ocean alkalinity and dissolved inorganic carbon (DIC) content would have required as much as 10^5 model years – an impossibly long simulation time given the level of complexity of the UVic model. Hence we extracted the model steady state after 10^4 years, but kept the background steady-state run ongoing concomitantly with the transient model simulation in order to correct the output of the latter based on changes in the former. Each transient simulation was forced with the historical natural and anthropogenic carbon emission for 200 years; at year 2000 an additional 5000 Pg C were emitted over one year (unless otherwise indicated), and carbon emissions were set to zero thereafter. All simulations were carried out for a period of ten millennia, ending at year 12,000.

A total of eight model versions were integrated to year 12,000, which we classified into three groups of experiments (see Table 1 for a description of all experiments). Group A (Section 3.1) experiments investigate the impact of the intensity and span of the prescribed carbon emissions. Simulation A0 is the basic emission scenario outlined in the above paragraph, and thus served as the main control run for this paper. Simulation A1 is similar but used a more conservative estimate of 1000 Pg C for future anthropogenic emissions. Finally, simulation A2 extended the carbon emission total of 5000 Pg over a much longer period: emissions were increased linearly until reaching double the current (year 2000) carbon emissions; the remaining carbon emissions were then distributed evenly during the period from 2050 to 3000, then set to zero thereafter. Although distributed over a longer period, the total carbon emissions remained unchanged from our control run A0.

Group B experiments (Sect. 3.2) compare the various model representations of the biological enhancement factor. In simulation B1, we replaced the NPP dependence term g(NPP) in

equations 14 and 15 with $g(CO_2)$ from equation 11 on all grid cells. Although carbon dioxide concentrations in the atmosphere are known to vary slightly across the surface of the Earth, in the UVic model pCO_2 is a global term with no defined spatial variability. This effectively removes the two-dimensionality of the biological feedback term, leaving temperature as the sole spatially-explicit variable. Runoff does not vary much unless there are major changes in hydrology or ice sheet distribution, neither of which were considered in our simulations. A further simplification was made in simulation B2 by removing the biological enhancement factor altogether and incorporating a parameterization that is only based on the temperature-dependent part of our spatially-explicit scheme.

Group C experiments (Sect. 4.3) compare the relative importance of carbonate and silicate weathering through their impacts on riverine fluxes of alkalinity and DIC. In simulation C1, we eliminated the silicate weathering feedback ($F_{Si} = f_{Si}$), leaving only the carbonate weathering part of the parameterization. Likewise, in simulation C2, the carbonate weathering feedback was negated ($F_{Ca} = f_{Ca}$), isolating the impact of the silicate weathering feedback. Finally, in model version C3 we eliminated both carbonate and silicate weathering feedbacks to maintain constant weathering fluxes (at steady-state values) throughout the simulation. This last model version effectively simulates the carbon sequestration potential of the oceans in the absence of the weathering feedback mechanism.

For each of the model versions outlined above (with the exception of C1 and C2), an identical setup was used with a zero-dimensional version of the weathering model whereby weathering rates were calculated based on global, rather than local changes in the control parameters (temperature, NPP, runoff); these 0-D model versions are identified in the figures using the "*" notation (for example, "A0*" refers to the zero-dimensional version of simulation A0). The code for these 0-D model versions was developed in an earlier study of terrestrial weathering changes with the UVic model [*Meissner et al.*, 2012].

3 Results

3.1 Group A results

The time series of CO₂ concentration in the atmosphere as well as weathering fluxes of carbon and alkalinity are shown in Figure 3a for each of the pulse (group A) scenarios (solid lines), and compared with results from similar scenarios using the 0-D version of the model (dotted lines). For all simulations, the 2-D model was always more efficient in removing CO₂ from the atmosphere than its 0-D counterpart. This can be partially explained by the initial global total weathering being slightly higher in the 2-D model (see Section 2.2.2); however, this cannot account for alkalinity weathering increasing nearly three times as much in the 2-D model as it does in the 0-D version (interestingly, 0-D weathering rates seem to be slightly higher than 2-D values for scenario A1). Instead, we propose that this is a natural consequence of using a twodimensional approach. Temperature, productivity, and runoff are closely related, as all three are positively affected by the increase in atmospheric CO₂: temperature from the greenhouse effect, NPP through the CO₂ fertilization of plants, and runoff as a result of both a temperature (hence precipitation) increase and the CO2-induced increase in plant water-use efficiency. Vegetation productivity also reacts positively to increases in temperature in extratropical regions, although this effect could be overcompensated for by an opposite reaction in tropical regions, where temperatures exceed the threshold for optimized plant growth [Matthews et al., 2005; Matthews et al., 2007]. This means that areas which see a large increase in one variable will more often than not see equally large increases in one or both of the other variables, further enhancing the local increase in weathering rates. A zero-dimensional model would not be able to create this effect because it uses globally summed or averaged variables. This is especially important with regards to temperature, as the global average would be dominated by oceanic SAT changes, which tend to be smaller than continental SAT changes.

Scenario A2, when compared to A0, suggests that the ability of the Earth system to recover from anthropogenic emissions is essentially independent of the rate at which the emissions occur. Atmospheric CO_2 concentrations recovered more slowly in the gradual emissions scenario at first since weathering fluxes were not increased as much, but the gap between the two curves gradually narrowed after A2 emissions ended at year 3000. We found a difference of 164 ppm in

atmospheric CO_2 concentration between A0 and A2 at year 12,000, which is nonetheless much greater than the difference between the pulse and IPCC A2 simulations in *Meissner et al.* [2012], in which a 5000 Pg C pulse was spread over 300 years. Given that the longer the carbon emissions are spread out over time, the longer it takes for atmospheric CO_2 levels to catch up to a pulse scenario, we can surmise that pulse scenarios would overestimate the ability of the weathering feedback mechanism to remove carbon from the atmosphere in the next several millennia, unless a way is found to mitigate anthropogenic emissions within the next century.

Time series of various carbon reservoirs for Group A scenarios are shown in Figure 3b. The ocean reservoir content at year 12,000 was nearly identical for scenarios A0 and A2, indicating that the ocean was even more indifferent to the rate of carbon emissions than the atmosphere. Zero-dimensional model ocean carbon exceeded the 2-D output at around year 8500 for scenarios A0 and A2, due to the fact that there was more carbon remaining in the atmosphereocean system. It is interesting that the land and sediment carbon reservoirs behaved differently from other reservoirs. The large carbon emissions (and associated temperature anomalies) in A0 and A2 appeared to have a counterproductive effect on land carbon content, which was not seen under the more modest temperature increase of simulation A1. If anything, this results points out the inability of the land reservoir to store any significant amount of excess carbon from the atmosphere on millennial timescales. Finally, the sediment carbon curve also behaved somewhat counterintuitively, as all three 2-D pulse scenarios produced a comparable increase of sediment carbon content, regardless of emission rate or amount of carbon released. For the 0-D model versions, total CaCO₃ buried mass increased more rapidly for scenario A1 despite lower amounts of carbon emitted. These results arise because carbon burial depends on a delicate balance which involves ocean temperature, alkalinity, and calcite concentration. Oceans in scenario A1 contained less CO₂ and CaCO₃, but were also cooler than in A0 and A2, which may explain why the total accumulation of CaCO₃ sediments was comparable between all three scenarios.

Global changes in surface air temperature, vegetation NPP, and surface runoff are shown in Figure 4 at various times during the 10,000 year simulation. As seen in Figure 4a, the most significant changes in temperature mostly occurred poleward of 60 degrees of latitude; however, there were also increases in many tropical regions. These results are to be expected given the static nature of wind fields in the UVic model, which prevent a reorganization of atmospheric

circulation and thus trap the warm anomalies in the tropics. Figure 4a (see also Figure 3c) also reveals that the cooling effects of carbon sequestration were not felt until well after year 3000, despite atmospheric CO_2 concentrations being decreased by nearly 1000 ppm between years 2000 and 3000; this is simply due to the thermal inertia of the ocean [*Matthews and Caldeira*, 2008]. By year 12,000, temperature anomalies across the globe became fairly uniform, with every area averaging 1-2°C warmer than pre-industrial state.

Changes in vegetation net primary productivity are shown in Figure 4b. Most of the world saw an increase in vegetation activity from the direct effect of CO_2 fertilization, with the exception of desert areas which remained the same (Africa, Asia) or become more arid (Australia). Changes in NPP also correlated well with changes in river runoff (Figure 4c); this is mainly a consequence of the effect of increased CO_2 concentrations on plants, which optimises vegetation water-use efficiency, leading to an increase in soil moisture and therefore runoff [*Nugent and Matthews*, 2012; *Cao et al.*, 2010]. The very large NPP increase in Indonesia around year 3000 was likely caused by the replacement of rainforest by the much more productive C4 grasses, and further enhanced by a 1000-year legacy of high CO_2 fertilization.

The resulting impacts of these changes in temperature, vegetation productivity, and runoff on CaCO₃ and CaSiO₃ weathering are shown in Figure 5. We found that changes in weathering were more strongly correlated to changes in NPP, and to a lesser extent, runoff. The influence of rock type distribution was also noticeable, especially on the carbonate/silicate weathering partitioning, while temperature had an overall modest impact. Most areas saw a moderate to high increase in both weathering types, with the exception of arid areas (deserts and ice caps) which experienced a minor decrease in weathering. The most significant change occurred in central western Asia (Kazakhstan), mirroring a moderate increase in vegetation productivity coupled with a considerable temperature change during the third millennium CE. The anomaly all but disappeared in later snapshots of the simulation, once global temperatures were no longer warm enough to sustain such high levels of vegetation productivity. Indonesia also saw a large increase in silicate weathering rates, on account of all three controlling parameters increasing by a large margin in the area, coupled with a predominantly silicate-heavy lithology. In later stages of the model simulation, weathering rate anomalies had mostly retreated to the tropical latitudes,

where productivity and runoff anomalies persisted the longest; elsewhere the increase in weathering rates was reduced to below 10% of their value during the third millennium CE.

3.2 Group B results

The purpose of this group of experiments was to assess the importance of including a parameterization for NPP (A0) rather than atmospheric CO₂ concentration (B1), or a weathering scheme based exclusively on temperature and runoff feedbacks (B2). Model output for atmospheric CO₂ concentration and weathering fluxes is shown in Figure 6a. The results strongly suggest that using vegetation productivity rather than CO₂ as a proxy for biological activity makes weathering fluxes much more sensitive to overall climate and environmental changes. Weathering fluxes peaked around year 2200, and the increase for simulation A0 (using NPP) was twice that for simulation B1 (using CO₂), and about three times larger than for simulation B2 (with no biological effect); in other words, adding a NPP dependence tripled the weathering increase compared to the case using a temperature dependence only. This is likely a result of rapid vegetation expansion in the high latitudes and the appearance of warm-adapted and more productive biomes in the temperate regions, which was taken into account in A0 but not in the Group B model versions. As a result, the recovery time of atmospheric CO₂ levels was much faster in A0, and vegetation productivity rapidly dropped below the levels of B1 and B2 (not shown). Interestingly, after year 7000 the weathering DIC flux in simulation A0 fell below that of B1, indicating that from that point onward the parameterization in B1was more effective in removing CO₂ from the atmosphere. This feature does not appear in the 0-D model results, where DIC weathering fluxes always remained higher in the productivity-dependent model version. As mentioned in section 3.1, it is possible that the increased effectiveness of the 2-D weathering parameterization (compared to 0-D) is caused by the coincidence of large temperature/runoff increases within areas that also see a large increase in vegetation NPP.

Figure 6b displays the time series of ocean and sediment carbon, as well as three parameters which are used to analyze the evolution of calcite sedimentation in the model: $CaCO_3$ production, pore layer portion, and dissolution. In contrast to 0-D versions of the model, there was a clear convergence of all three 2-D curves for ocean carbon content resulting from a substantial drop in weathering rates during the latter half of the simulation period. The rate of increase of CaCO₃ buried mass was slower in model versions with lower weathering rates; this

surprisingly differs from Fig 3b where there was not much difference between the three model versions. However, the 0-D curves still displayed a significant lag behind their 2-D counterparts. The pore layer portion remained unchanged during the first thousand model years after the introduction of the 5000 Pg C pulse, thus mirroring the results of *Meissner et al.* [2012]. Higher biological activity and carbonate concentration in the surface ocean due to warmer temperatures was found to lead to a sharp increase in calcium carbonate formation and precipitation; this was balanced by a rising of the carbon compensation depth (CCD) in the deep ocean fueled by the rising acidity of the ocean, which increased the overall dissolution rate of calcite. As the more immediate effects of the carbon emission pulse receded, oceans became cooler and calcite formation weakened, while dissolution kept increasing for another 1000 years. This created an imbalance in the CaCO₃ pore layer fraction which appears from year 4000 onward. Note that even though dissolution rates in CaCO₃ buried mass due to the enormous increase in oceanic carbon content.

Figure 7 displays the spatial distribution of CaCO₃ and CaSiO₃ weathering changes at various points of the simulation timeline for model version B1. Several areas of higher weathering from Figure 5 were completely absent (central Eurasia), and some others were greatly reduced (tropical Africa). These are the most important examples of how the vegetation productivity parameterization can greatly enhance carbonate weathering locally, and silicate weathering worldwide (see Figure 4b). Weathering rates were generally higher in A0 throughout the simulation, but it should be noted that in some areas in the final snapshot (year 12,000 CE) weathering in A0 fell below that of B1. Since the only difference between B1 and B2 is the presence of (globally averaged) atmospheric CO_2 concentration as a factor, the equivalent figure for model version B2 (not shown) would have been extremely similar to B1.

3.3 Group C results

The purpose of this group of experiments was to isolate and compare the individual contributions of carbonate (C1) and silicate (C2) weathering to the global feedback mechanism, and to compare them with a scenario where this negative feedback does not exist (C3). The time series of atmospheric CO₂ concentrations and DIC/alkalinity weathering are shown in Figure 8a. After 500 years of roughly similar behavior, the curves diverged into three distinct narratives. By year

12,000, about 33% of the emitted carbon was still in the atmosphere for model version C3 (constant weathering), whereas about 20% of the carbon remained for the C1 (change in carbonate weathering only), and 10% for C2 (change in silicate weathering only) and A0 (control run). This is due to the immediate effect of carbonate weathering, which increase alkalinity content in the ocean faster than the rate at which the precipitation of calcium carbonate increases. Over timescales of 10^5 years or more, we would expect the C3 curve to catch up to C1 as increased calcite burial releases carbon dioxide back to the ocean, negating the carbon removal at the surface; this outcome is verified in the million-year simulations of *Colbourn et al.* [2013] but impossible to replicate here due to the time scales involved. The C2 model version yielded very similar results to A0, which included the impacts of both carbonate and silicate weathering. The difference between the two was greater initially, as the additional alkalinity provided by carbonate weathering further enhances the oceanic uptake of CO₂ from the atmosphere, but the gap gradually narrowed as the medium-term impacts of carbonate weathering faded away. Again this outcome is verified over geologic timescales by Colbourn et al. [2013], with both the A0 and C2 equivalents returning the Earth system to pre-industrial levels. There was no change in DIC weathering output from C2 since silicate weathering in this model does not increase the DIC flux to the ocean. Alkalinity flux from C1 exceeded that of other model versions towards the end of the simulation period as the slower carbon removal resulted in much warmer surface conditions compared to other model versions.

The evolution of ocean sedimentation is presented in Figure 8b using five model variables: ocean carbon, calcite buried mass, upward/downward flux of calcite, and pore layer portion. Ocean carbon levels remained similar between C1 and C2 during the first two thousand years, after which C1 overtook C2 and eventually A0, despite resulting in the least amount of carbon removal of the three model versions. This is because C1 would send as much DIC into the ocean as alkalinity, which is counterproductive to atmospheric carbon removal. Conversely, C2 removed almost as much carbon as A0 while adding 1000 Pg C less into the ocean, testifying towards the efficiency of silicate weathering in removing carbon from the atmosphere compared to carbonate weathering. Calcite sedimentation followed a very similar evolution to the experiments in Group B (section 3.2), with the calcite pore layer portion remaining unchanged for 1000 years until the upward flux of calcite (dissolution) became larger than the downward flux of calcite (production/precipitation). Here it becomes clear that rock weathering, and in

particular, silicate weathering, is crucial in maintaining the stability of the pore layer fraction in the long term. Model version C3, where weathering rates remain constant, produced a much sharper increase in calcite dissolution compared to A0, where both weathering types respond to changes in climate, and the burial of $CaCO_3$ in sediments occurred much faster in A0 than in C3. Additionally, pore layer portion was better maintained by silicate weathering (C2) than carbonate weathering (C1). These results suggest that the alkalinity flux supplied by silicate weathering is necessary not only for decreasing the oceanic buffer factor (i.e., the concentration of carbonic acid and carbonate in ocean surface water) and allowing the uptake of more CO_2 from the atmosphere, but also to maintain a better balance of the oceanic sedimentary pore layer by mitigating the increase in calcite dissolution in the deep compared to the production rate in the surface layer.

4 Discussion

The weathering scheme introduced here is subject to some caveats relating to the formulation itself, as well as the limitations inherent in the UVic model. *Colbourn et al.* [2013] carefully discuss the potential misrepresentation of temperature as a factor, especially when other parameters such as vegetation productivity are also taken into account. In particular, it is possible that the temperature dependency for carbonate weathering (equation 7), which was developed empirically from correlating groundwater $CaCO_3$ concentration with water temperature in various river catchment basins, also captures the coincident changes in vegetation productivity and river runoff, hence making the other factors redundant to a certain extent. Whether this would introduce a significant error to the modeling is questionable, as temperature on its own was shown to have at most a moderate impact on overall changes in weathering rates (see Sect. 3.1).

The validity of the other two parameterizations – NPP and runoff – is difficult to assess as the formulations are based on the arbitrary assumption that weathering rates vary monotonically and linearly with changes in the two parameters. In the case of productivity dependence, for example, the parameterization is meant to represent the physical impacts of root expansion, and the chemical impacts of soil kinetics, on the breakdown of rock into minerals and their eventual dissociation by carbonic acid. Thus an ideal productivity scheme would account for the impacts

of various plant types on each of the lithologies in terms of areal coverage, root expansion, and other relevant quantities. Moreover, it should be noted that both the NPP and runoff schemes in our model rely heavily on the ratio between initial weathering and initial NPP/runoff, meaning that a change in a parameter in an initially low-activity region (such as colder climates) may have a disproportionately higher impact on weathering rates compared to changes in tropical areas. It is possible that the introduction of vegetation in a previously non-vegetated area would introduce a stress likely to drastically increase rock weathering, but this is an effect that would be better represented by directly parameterizing the new plant type as a stress on the underlying lithology. Therefore, a better parameterization may be one based on the absolute value of NPP/runoff (using for example, a non-linear empirical function linking weathering rate and net primary productivity) rather than the ratio of the current value to the initial value. The development of such a relationship, however, would require a more in-depth investigation of the role of plants, and biotic activity in general, on the physical and chemical weathering of rocks.

Another source of uncertainty in our results lies in the UVic model itself. While very well suited to simulate long-term impacts of carbon emissions and increased weathering rates on ocean biogeochemistry, on a shorter time scale $(10^2-10^3 \text{ years})$ the lack of advanced atmospheric dynamics prevents the model from adapting to the extreme warming brought on by carbon emissions in a manner consistent with our understanding of global climate. Under extreme warming there is a poleward shift of the tropical and subtropical cells and consequent changes in precipitation patterns, leading to a potential overestimate of atmospheric temperature and moisture content changes over tropical regions (see Sect. 3.1). This effect is important mostly between years 2000-3000 CE, and fades away as the brunt of the climate and biogeochemical changes are shifted to the oceans. The model's simplified precipitation scheme also likely affects its ability to simulate runoff changes, which are central to both the initiation and modulation of weathering rates.

Terrestrial rock weathering is a complex mechanism with many variables worth considering, many of which have a high degree of interdependence. In the scheme introduced in this paper for the UVic model, we considered the impacts of temperature, productivity and runoff (all parameters previously examined in zero-dimensional weathering models), along with lithological distribution to drive spatial variability. However, many other factors which affect weathering

rates were unaccounted for that could also be relevant in the context of a spatially explicit weathering scheme. Perhaps the most meaningful of all is the consideration of sea level change. It is highly likely that the extreme warming caused by anthropogenic emissions would result in a significant melting of the Greenland and West Antarctic ice sheets [*Clark et al.*, 2016], not only disrupting the freshwater balance in the polar oceans, but also greatly contributing to a global rise in sea levels along with the thermal expansion of seawater. Many of the low-elevation continental shelves threatened by sea level rise are situated in weathering active, tropical regions, and therefore the interruption of terrestrial weathering due to the flooding of these areas could substantially reduce the global weathering output, thus weakening the response to global warming. Note that the extensive warming could also bring about a decrease in ice sheet area, especially in Greenland, which would open up some potentially very active weathering regions [*Kump and Alley*, 1994]. However, the extent of this areal reduction of ice sheet cover over a few thousand years is likely to be overwhelmingly compensated by the area of land flooded by sea level rise.

Another factor of some relevance is the interaction with land biogeochemistry. There has been an extensive discussion in recent years on the role of mid- to high-latitude peatlands in the context of a rapidly warming Earth, especially with regards to the decarbonation of these ecosystems and subsequent release of greenhouse gases in the atmosphere that could greatly amplify global warming. While the release of methane by itself does not directly affect terrestrial weathering, there are a variety of soil processes within peatlands which are triggered or amplified by warming and which would have a significant local effect on the chemical dissociation of rocks.

There are many other factors which would be worth investigating. For example, a distinction between physical and chemical weathering would allow the inclusion of factors such as altitude, as wind and relief/slope play a major role in physical weathering. The impact of ground frost at higher latitudes also leads to erosion, and could increase weathering rates in colder climates. Finally, one cannot ignore anthropogenic impacts, in particular the spread of modern agriculture, in which crop yields are often boosted using mineral fertilisers and other chemicals, which mix in with the soil water and accelerate the erosion of the bedrock. Other features of the Anthropocene worth mentioning include acid rain and land use change, all of which need to be

taken into consideration in order to better represent the modern dynamics of global biogeochemistry. Unfortunately, it is unlikely that most of these factors can be properly integrated in current low- and intermediate-complexity climate models, on account of their requiring a spatial resolution much finer than what most EMICs can offer. For example, the UVic model's $1.8^{\circ} \times 3.6^{\circ}$ resolution cannot resolve physical mechanisms which occur over a single-kilometer spatial scale.

5 Conclusions

A spatially-explicit weathering scheme has been developed and integrated into the University of Victoria Earth System Climate Model (UVic ESCM). The model was constructed in such a way that weathering rates at a certain point are computed based on the difference in temperature, vegetation net primary productivity, and runoff, between that point and pre-determined initial conditions. In our model, those initial conditions were based on pre-industrial runoff and lithology [*Amiotte-Suchet et al.*, 2003], which provides the basis for the two-dimensionality of the model.

The model was tested with scenarios of future climate change, using (in most cases) a pulse of 5000 Pg C at year 2000 to simulate climate system recovery from anthropogenic emissions and the role of global weathering during the following 10000 years. Overall, the model results suggested that weathering has a negligible effect on atmospheric CO_2 and ocean biogeochemistry on short timescales, but its impact becomes more discernible as we progress to multimillennial timescales. We also found that climate system recovery from carbon emissions was much faster using a two-dimensional model rather than the zero-dimensional model versions used in previous work. Among the various climate factors used in the model, we found primary productivity to be by far the most important, producing an increase in global weathering far higher than a model version using atmospheric CO_2 levels to represent biotic activity, or one where only temperature and runoff changes were considered. This highlights the need for further research to determine whether this effect of biotic activity on physical and chemical weathering is in fact an important real-world process that is independent of temperature and/or runoff change. Lithology itself was also found to be very important, often meaning the difference between a weathering-active and high- and low-weathering region. In terms of global totals, carbonate weathering was found to

be more prominent than silicate weathering, mostly on account of weathering-vulnerable rocks being mostly carbonate-weathered. However, our results clearly emphasized that silicate weathering is the only process of the two which has the capacity to fully restore the climate system to pre-industrial levels (on timescales of 10^5 years), thus confirming the findings of *Colbourn et al.* [2013].

This work has established the importance of using a spatially-explicit weathering scheme to better represent long-term changes in carbon biogeochemistry. Our approach, although crude, has demonstrated that weathering can be integrated on the grid-cell level and still produce reasonable results. This study did not take into account the more subtle aspects of spatial variability, such as the impacts of ice sheets, sea level changes, and local factors such as soil activity and topography. These are therefore important processes to include in further analyses of the effect of deglacial weathering changes on ocean biogeochemistry and climate change.

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Lithology	k	α	
Carbonate rocks	1.586	0.93	
Shales	0.627	0.39	
Sands and sandstones	0.152	0.48	
Basalts	0.479	0	
Shield rocks	0.095	0	
Acid volcanic rocks	0.222	0	

Table 1. Rock type constants used in equations 5 and 6. Here, *k* represents the weathering rate multiplier, with a higher multiplier signifying a higher concentration of weathering products per unit of runoff (or alternatively, a lower resistance to weathering agents); α denotes the fraction of the given rock type to weather as carbonate rocks. A value of zero means that the rock type consists of silicate minerals only.

Group	Experiment Name	Emission total (Pg C)	Emission period (years CE)	Biological parameter	CaCO ₃ weathering switch	CaSiO ₃ weathering switch
A	A0	5000	2000-2001	NPP	ON	ON
	A1	1000	2000-2001	NPP	ON	ON
	A2	5000	2000-3000	NPP	ON	ON
В	B1	5000	2000-2001	Atm. CO ₂	ON	ON
	B2	5000	2000-2001	None	ON	ON
С	C1	5000	2000-2001	NPP	ON	OFF
	C2	5000	2000-2001	NPP	OFF	ON
	C3	5000	2000-2001	NPP	OFF	OFF

Note: The "*" notation refers to zero-dimensional versions of the model using otherwise identical experimental parameters.

Table 2. Description of each experiment carried out in this study. The emission total is the total amount of carbon emitted by the pulse starting at year 2000, while the emission period represents the time span of the pulse; the emission total is divided equally among the number of time steps during the emission period. For the biological factor, "NPP" refers to equation 10, "Atm. CO_2 " to equation 11, and "None" signifies that this part of the weathering scheme is ignored. Finally, when the CaCO₃ switch is OFF, the amount of carbonate weathering produced by the model is set to its pre-industrial value for the duration of the simulation; similarly for when the CaSiO₃ switch is OFF.

(a)



(b)



Figure 1. Distribution of the six major rock types for the present day. Presented here are (**a**) its adaptation to the UVic model in $3.6^{\circ} \times 1.8^{\circ}$ resolution, displaying only the dominant lithology in each grid cell; and (**b**) the interpolated rock type fraction in each grid cell. For the latter, the data is shown ranging from 0 (white) to 1 (full color).

(a)



(b)



Figure 2. Pre-industrial (year 1800 CE) setup for our weathering scheme. (**a**) Model simulated annual mean river runoff, which is combined with rock type fractions (Figures 1 (b) and (c)) using equations 5 and 6 to produce (**b**) the carbonate and silicate weathering fluxes at pre-industrial steady-state. Note the non-linear color scales, used here to better display values outside of tropical regions.







Figure 3. Time series of simulated changes in various globally-averaged or summed model outputs for Group A scenarios, compared with pre-industrial steady-state values. These scenarios include **A0** (high-amplitude pulse), **A1** (low-amplitude pulse), **A2** (gradual emissions), and their zero-dimensional counterparts (indicated by the "*" symbol). Shown here are (from top to bottom): (**a**) atmospheric CO_2 concentrations, and weathering fluxes of DIC and alkalinity; (**b**) global carbon budgets for atmospheric, ocean, land, and sediment reservoirs; and (**c**) surface air temperature, net primary productivity, and oceanic concentrations of DIC and alkalinity. Note the different scales along the time axis (separated by vertical dashed black lines). The curves shown here represent experiments A0 (red), A1 (blue), and A2 (green), with dashed colored lines representing the zero-dimensional equivalent model version.

(a)



(b)



Vegetation net primary productivity: difference from pre-industrial state



2100 CE 3000 CE

River runoff: difference from pre-industrial state



Figure 4. Spatial distribution of changes in (**a**) surface air temperature; (**b**) vegetation net primary productivity; and (**c**) river runoff for experiment A0 from pre-industrial (year 1800 CE) state to years 2100, 3000, 6000, and 12000 CE. Non-linear color scales are used in panels (b) and (c) to better display the results for the later stages of the model simulation.



Figure 5. Spatial distribution of changes in carbonate $(CaCO_3)$ and silicate $(CaSiO_3)$ weathering for experiment A0 from pre-industrial (year 1800 CE) steady-state to years 2100, 3000, 6000, and 12000 CE. Note the non-linear color scale, used to better display values during the later stages of the model simulation.

weathering flux difference from pre-industrial state





Figure 6. Time series of simulated changes in various model outputs for Group B scenarios, compared with pre-industrial steady-state values. These scenarios include A0 (dependence on temperature, NPP, and runoff), B1 (dependence on temperature, atmospheric CO₂, and runoff), B2 (dependence on temperature and runoff only), as well as their zero-dimensional counterparts (indicated by the "*" symbol). Shown here are (from top to bottom): (a) atmospheric CO₂ concentrations, and weathering fluxes of DIC and alkalinity; and (b) oceanic carbon budget, sediment carbon budget, downward flux of calcite into sediments, calcite pore layer portion, and dissolution of calcite in sediments. Note the different scales along the time axis (separated by vertical dashed black lines). The curves shown here represent experiments A0 (red), B1 (blue), and B2 (green), with dashed colored lines representing the zero-dimensional equivalent model version.


weathering flux difference from pre-industrial state

Figure 7. Spatial distribution of changes in carbonate (CaCO₃) and silicate (CaSiO₃) weathering changes for experiment B1 between pre-industrial steady-state (year 1800 CE) and years 2100, 3000, 6000, and 12000 CE. Note the non-linear color scale, used to better display values during the later stages of the model simulation.





Figure 8. Time series of simulated changes in various model outputs for Group C scenarios, compared with pre-industrial steady-state values. These scenarios include **A0** (both weathering types active), **C1** (carbonate weathering only), **C2** (silicate weathering only), **C3** (no weathering), as well as the zero-dimensional counterparts to C0 and C3 (indicated by the "*" symbol). Shown here are (from top to bottom): (a) atmospheric CO_2 concentrations, and weathering fluxes of DIC and alkalinity; and (b) oceanic carbon budget, sediment carbon budget, downward flux of calcite into sediments, calcite pore layer portion, and dissolution of calcite in sediments. Note the different scales along the time axis (separated by vertical dashed black lines). The curves shown here represent experiments A0 (red), C1 (blue), C2 (green), and C3 (black), with dashed colored lines representing the zero-dimensional equivalent model version (when available).

Chapter 5

Long-term implications of the terrestrial weathering feedback mechanism on projected future global temperature and sea level changes

In Chapter 3, we described a set of experiments using box-model parameterizations of weathering in order to assess the changes in global weathering intensity over the course of the last deglacial period. We ultimately concluded that a two-dimensional weathering scheme would be necessary in order to resolve the more spatially-explicit aspects of glacial weathering, notably in terms of sea level rise and the flooding of continental lowlands. In Chapter 4, we then proceeded to develop this two-dimensional weathering, but in the context of future climatic changes, the premise being that excessive warming over the next several millennia could severely reduce the volume of ice over Greenland and Antarctica, with the associated consequences of the global sea level. This chapter is based on a manuscript in preparation by authors Brault, M.-O., Matthews, H.D., and Mysak, L.A., which is planned for submission to the journal Geophysical Research Letters.

Long-term implications of the terrestrial weathering feedback mechanism on projected future global temperature and sea level changes

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ABSTRACT

In this paper, we apply a spatially-explicit weathering parameterization to the investigation of future climate changes, following scenarios of representative carbon pathways as presented in the latest IPCC reports. Following on an earlier study which examined the millennial implications of global warming on sea level rise, we come up with a revised assessment of sea level rise taking into account the effect of increased weathering rates on global climate recovery. Based on our model results and interpretation of the impact of temperature on ice sheet melting and sea level rise, we surmise that the impact of rock weathering will not be fast enough to prevent excessive melting of polar ice caps during the next several millennia despite bringing about a much quicker recovery of atmospheric CO_2 levels and surface air temperature to pre-industrial levels.

1 Introduction

It is well-established that the legacy of anthropogenic increases in greenhouse gases in the atmosphere, especially carbon dioxide (CO₂), will extend well beyond the end of the present century. However, the consequences for long-term future climates are poorly constrained due to a lack modeling studies which go beyond a few centuries, as well as a relatively limited understanding of the mechanisms which will drive an eventual removal of carbon residing there from anthropogenic activities. This is especially true when estimating the amplitude of future sea level changes and their implications on socioeconomic and environmental challenges ahead [*Clark et al.*, 2016].

The removal of anthropogenic carbon from the atmosphere is driven on the short term by ocean uptake, on intermediate timescales by the ocean biological pump and carbonate burial, and on the long term by silicate rock weathering [*Ridgwell and Hargreaves*, 2007; *Eby et al.*, 2009]. This long residence time, coupled with the thermal inertia of the climate system, means that the greenhouse gas emissions of the past century have already committed the Earth to millennia of global warming, and the amplitude and longevity of these changes, notably in terms of polar ice melting and global sea level rise, will depend on the mitigation efforts and resulting emission pathway of the next several decades.

A number of studies have addressed the consequences of anthropogenic carbon emissions and the multi-millennial lifetime of its perturbation on the climate system. The scientific literature generally puts the lifespan of the anthropogenic carbon perturbation to be on the order of 10^5 years, with values of 200 kyr [*Archer et al.*, 1997] and 400 kyr [*Berner and Kothavala*, 2001; *Archer*, 2005] most commonly cited; however, permanent land-use changes may indefinitely alter the equilibrium atmospheric CO₂ concentration [*Walker and Kasting*, 1992]. The issue has also been addressed using intermediate-complexity models. *Montenegro et al.* [2007] found that a positive feedback from the land carbon reservoir might further enhance the anthropogenic perturbation, while *Uchikawa and Zeebe* [2008] confirmed that weathering feedbacks do not operate on sub-millennial time scales, and thus cannot mitigate the rise in atmospheric pCO₂ and ocean acidification during the next several centuries. They also distinguished feedbacks from carbonate and silicate weathering, noting that the latter only becomes dominant on time scales of 10^5 years or greater. Archer et al. [2009] compared the output of several EMICs (including an earlier version of the UVic ESCM), which generally agreed on a residence time of atmospheric CO₂ of several tens of thousands of year. However, they noted that this value is inherently dependent on the timescale of CO₂ neutralization by silicate weathering, which is still poorly constrained and difficult to investigate with intermediate complexity models.

In this study, we use an Earth system Model of Intermediate Complexity (EMIC) coupled with a spatially explicit weathering scheme [*Brault et al.*, 2016] to constrain changes in rock weathering rates in future climate change scenarios and assess its importance for anthropogenic carbon sequestration over the next several millennia and its implications on global climate and sea level rise. Forcing data from the various representative constant pathway (RCP) scenarios (IPCC, 2013) were used to drive the model according to various documented projections of future climate changes. Although rock weathering changes are typically irrelevant on sub-tectonic time scales (10^5-10^6+ yr) and are therefore mostly ignored in assessments of future climate changes, the severity of the projected CO₂ level increases and global warming have been shown to be sufficient for terrestrial weathering to substantially accelerate the recovery of the Earth system on multi-millennial timescales [*Lenton and Britton*, 2006].

2 Model description

Global climate in this study was computed using version 2.9 of the University of Victoria Earth System Climate Model (UVic ESCM), an intermediate complexity coupled atmosphere / ocean / sea-ice model with integrated land surface and vegetation schemes [*Weaver et al.*, 2001]. Its main component is version 2.2 of the GFDL Modular Ocean Model (MOM), a three-dimensional ocean general circulation model with 19 uneven vertical levels [*Pacanowski*, 1995], which is coupled to a vertically integrated energy-moisture balance atmosphere model [*Fanning and Weaver*, 1996], a dynamic-thermodynamic sea-ice model [*Bitz et al.*, 2001], and the land surface / vegetation module MOSES-2/TRIFFID [*Cox et al.*, 1999]. It also includes organic [*Schmittner et al.*, 2008] and inorganic [*Ewen et al.*, 2004] exchanges of carbon within the atmosphere-ocean system and between land reservoirs [*Matthews et al.*, 2005]. The model is driven in the short term by seasonal variations in solar insolation and wind fields [*Kalnay et al.*, 1996], and in the long-term by orbital parameter changes [*Indermühle et al.*, 1999].

Changes in weathering rates were computed using the spatially explicit scheme developed by *Brault et al.* [2016]. The model follows the lithological paradigm of *Amiotte Suchet et al.* [2003], which classifies the world's rocks into six categories and assigns one to each land grid cell based on the dominant lithology in the area which it covers. Preindustrial (year 1800) weathering rates on each grid cell are calculated based on the empirical properties of the assigned rock type as well as runoff. Weathering rates are then re-evaluated at the end of each model year based on local changes in temperature, vegetation productivity, and runoff, and the global sum is fed to the model's ocean biogeochemistry module as riverine fluxes of alkalinity and dissolved inorganic carbon.

3 Methods

Preindustrial steady-state (year 1800) conditions were obtained by integrating the model for 20,000 years; we used the same steady-state as in *Brault et al.* [2016]. In order to reproduce the IPCC scenarios as faithfully as possible, we imported data for the UVic Model used in the EMIC-AR5 project. The model was forced with historical data for atmospheric CO_2 concentrations, non- CO_2 greenhouse gas forcings, land-use changes and sulphate aerosol optical depth between the years 1800 and 2005, and subsequently with their projected evolution from year 2005 through year 2300. In order to avoid inconsistencies, values for sulphate and non- CO_2 GHG forcings were calculated to linearly decrease from their projected value at year 2105 to reach zero at year 2300. A first set of three simulations were carried to year 2300 – one for each of the RCP scenarios: RCP2.6, RCP6.0, and RCP8.5 – in order to calculate the level of CO_2 emissions necessary to follow the atmospheric CO_2 curve. The three RCP scenarios were then simulated again from year 1800 through year 12,000, this time using the anthropogenic CO_2 emissions as forcing rather than atmospheric CO_2 conditions.

In this study, we calculated sea level rise based strictly on the increase in global temperature. For each of the RCP scenarios examined we linked the rise in sea level associated with meltwater fluxes from the three major contributors – glaciers, Greenland, and Antarctica – to the accumulated degree-years of temperature anomalies in a previous set of results with version 2.9 of the UVic ESCM [*Clark et al.*, 2016]; the effect of thermal expansion on sea level was

computed explicitly in the UVic model. Contributions from each of those four sources were added together to obtain the total sea level rise for a given year.

4 Results and discussion

Our findings are summarized in Figure 1: the top and middle panels display the timeseries of atmospheric CO₂ concentrations and surface air temperature, respectively, and changes in global sea levels are shown in the bottom panel. Whereas in the model simulations carried out by *Clark* et al. [2016] temperature rose sharply following the anthropogenic carbon emissions period and remained relatively constant thereafter, our model output with the effect of rock weathering showed a clear decreasing trend of the globally averaged surface air temperature starting at year 3000 CE. For example, in the RCP8.5 scenario, globally averaged temperature decreased from a high of 21°C to around 15°C by year 12000, whereas they remained relatively constant at 20°C according to the model output of Clark et al. [2016]. A similar decrease in global temperatures was observed for scenario RCP6.0. Our model output for RCP6.0 suggests a hiatus in the global cooling between years 3500 and 4500 due to a sudden loss of sea ice around Antarctica; this is likely a result of a change in Antarctic deep water formation in the model, although the validity of such an event is questionable as it doesn't seem to occur in neither RCP2.6 or RCP8.5. Finally, in our RCP2.6 model run, temperature was found to recover extremely quickly (within a few hundred years), with global temperatures well on their way to preindustrial levels by year 12,000. These results are similar to those obtained by Brault et al. [2016] in their non-RCP future climate change simulations, and suggest that, in cases of large anthropogenic carbon emissions, weathering feedbacks on climate are poised to be an important player in future climates over millennial scales.

The impacts of weathering on surface air temperature are reflected in the resulting change in global sea level, although the differences between our results and those of *Clark et al.* [2012] are not as significant as the temperature response to weathering changes. The most noticeable difference comes from scenario RCP2.6, in which any rise in sea level due to ice sheet melting is effectively negated, leaving thermal expansion as the sole contributor to changes in sea level. This difference is unlikely to be caused by the introduction of weathering in the model, however, as the recovery of global surface air temperature and atmospheric CO_2 concentrations is too rapid

to have been triggered by changes in weathering; rather, it highlights the differences in scenarios between the two studies. For scenarios RCP6.0 and RCP8.5, the impact of weathering slows the sea level rise by approximately 5 meters by the year 12,000. As glaciers and the Greenland ice sheet are both completely melted within the 10 millennia of the model simulation, this difference comes exclusively from a slower melting of the Antarctic ice sheet. This relatively small difference is not unexpected, however. Most of the ice sheet melting occurs during the first 2-3 millennia of the model run, when weathering does not have much of an impact. Although the negative feedback mechanism does substantially accelerate the recovery of CO_2 levels and temperature to pre-industrial levels, global temperatures remain above present day levels throughout all of the simulations. When also taking into account the positive feedback mechanism triggered by the decreasing albedo and altitude, it is unlikely that ice sheet melting could be reversed by a more rapid decrease in temperature.

Several aspects of the interactions between weathering and glaciers have been overlooked so far. The rise in sea level due to meltwater flux and thermal expansion would lead to coastal flooding all around the world, thus slightly decreasing the land surface area. The resulting decrease in global weathering intensity would likely not be compensated by the small gain in land area from the receding ice sheets. However, the areas uncovered by the melting ice would have extremely brittle and weathering-sensitive rocks from millennia of pressure under the ice; exposing these areas to the elements could drastically increase the weathering output in those grid cells. Therefore, future work should focus on resolving the two-dimensional aspects of glacial melting and the associate sea level rise.

5 Conclusions

A spatially-explicit weathering scheme was used to simulate representative carbon pathway (RCP) scenarios of future global warming. The model was coupled to a linear approximation of temperature impacts on ice sheet melting and the associated increase in sea level, which was based on the previous results of *Clark et al.* [2016]. We found that including changes in global weathering intensity as a dynamic component of the model could greatly influence the behavior over the next several thousand years in simulations of future climates, with the difference in globally averaged temperatures being as high as 5°C between a model version with weathering

and one without. The impacts on sea level were relatively benign, however, and taking into account changes in weathering only limited sea level rise by 5 meters over the next 10,000 years, compared to the results of *Clark et al.* [2016].

This work has demonstrated the importance of including weathering as a feedback mechanism during any climate model simulation involving rapid changes in environmental conditions. This study did not take into account the more subtle aspects of spatial variability, such as the impacts of ice sheets, or sea level changes. These are therefore important processes to include in further analyses of the effect of deglacial weathering changes on ocean biogeochemistry and climate change.



Figure 1. Time series of simulated changes in various globally-averaged or summed model outputs for a range of representative carbon pathway (RCP) scenarios, including RCP2.6 (black), RCP6.0 (green) and RCP8.5 (red). Shown here are (from top to bottom): atmospheric CO_2 concentrations; globally averaged surface air temperature; and changes in global sea level. Note the different scales along the time axis (separated by vertical dashed black lines).

Chapter 6 Concluding Remarks

1 Summary

The objectives of this thesis were to (1) investigate changes in global weathering intensity during the last deglacial period and during future climatic changes; and (2) develop a spatially-explicit weathering scheme based on the heterogeneous distribution of lithologies across the world, and apply it to the same periods of interest in order to compare the results with the output from the 0-D model. Using the modeling tools provided by *Meissner et al.* [2012] and the work of *Colbourn et al.* [2013] as a precedent, we developed a two-dimensional weathering parameterization based on the rock distribution paradigm introduced by *Amiotte Suchet et al.* [1995; 2003]. Although this thesis has focused mostly on the development and testing of this model, the weathering scheme itself can be used to investigate several aspects of past and future climatic and carbon-cycle changes.

In Chapter 3, we examined the effect of deglacial weathering changes on ocean biogeochemistry and atmospheric CO₂ using a set of box model parameterizations of weathering fluxes within the UVic ESCM; these parameterizations depended on temperature, atmospheric CO₂ concentration, and vegetation production. Changes in riverine alkalinity and DIC fluxes were examined for the period starting at the end of the last glacial period (16,000 BCE) through to the mid-Holocene (4,000 BCE); in those transient model simulations, changes in global climate were driven by observed atmospheric CO₂, ice sheet configuration, and orbital parameters. Our model simulations yielded alkalinity DIC flux increases ranging between 0.063-0.126 Pg C/yr and 0.024-0.044 Pg C/yr, respectively, between glacial and Holocene conditions. Differences between the various model versions showed a biological enhancement of weathering: including vegetation productivity rather than atmospheric CO₂ as a proxy for biological activity resulted in much larger increases in global weathering intensity, indicating the importance of obtaining a better understanding of the effect of deglacial vegetation dynamics on the rock cycle. In a second set of experiments, the increases in alkalinity and DIC fluxes obtained from the transient model simulations were inserted into the model at specified time points (10,000 BCE and 15,000 BCE) in order to estimate the effect of these weathering changes on atmospheric CO_2 levels. Individual contributions of alkalinity and DIC were separated from one another as well as from the other external forcings (ice sheet distribution and orbital parameters). Carrying out the model run for 8000 years resulted in a decrease of atmospheric CO_2 concentrations of approximately 16.5 ppm at 10,000 BCE weathering levels, and about half as much at 15,000 BCE conditions. The individual contributions of alkalinity and DIC were substantial and of opposite direction; where DIC inputs alone led to a net loss of carbon from the ocean to the atmosphere, alkalinity inputs by themselves stimulated a significant CO_2 uptake into the ocean. These two effects combined relatively linearly, resulting in a net increase in ocean carbon (and associated atmospheric CO_2 consumption) from increased weathering. Based on the different effects of carbonate and silicate weathering on alkalinity and DIC fluxes, these results suggest that the spatial distribution of rock lithology influences the strength and efficiency of weathering as a feedback mechanism on global climate.

In Chapter 4, we tested our newly-developed spatially explicit weathering scheme in scenarios of future climate changes. In most cases, a pulse of 5000 Pg C at year 2000 was used to examine climate system recovery from anthropogenic emissions and the role of global weathering during the following ten millennia. Overall, the model results suggested that weathering has a negligible effect on atmospheric CO₂ and ocean biogeochemistry on short timescales; weathering becomes more discernible on multimillennial timescales. We also found that climate system recovery from carbon emissions was much faster with the two-dimensional model than with the zero-dimensional model versions used in previous work. Among the various climate factors used in the model, we once again found primary productivity to outmatch the others in its relative importance, yielding far greater changes in weathering intensity compared to model versions using a different parameterization for biological enhancement. Lithology itself was also found to be very important, as the difference in chemical reactivity between the different rock types is quite important. In terms of global totals, carbonate weathering was found to be more prominent than silicate weathering, mostly on account of weathering-vulnerable rocks being mostly carbonate-weathered. However, our results clearly emphasized that silicate weathering is

the only process of the two which has the capacity to fully restore the climate system to preindustrial levels (on timescales of 10^5 years).

2 Future work

Terrestrial rock weathering is a complex mechanism with many variables that can be considered, many of which have a high degree of interdependence. In the scheme developed in this thesis for the UVic model, we considered the impacts of temperature, productivity and runoff, all parameters previously examined in zero-dimensional weathering models, and lithological distribution to drive spatial variability. However, many other factors which affect weathering rates were unaccounted for; these could become especially relevant in the context of a spatially explicit weathering scheme. Perhaps the most meaningful of all is the consideration of sea level change. It is highly likely that the extreme warming caused by anthropogenic emissions will result in a significant melting of the Greenland and West Antarctic ice sheets [Clark et al., 2016], not only disrupting the freshwater balance in the polar oceans, but also greatly contributing to a global rise in sea levels on top of that caused by the thermal expansion of seawater. Many of the low-elevation continental shelves threatened by sea level rise are situated in weathering-active, tropical regions, and therefore the interruption of terrestrial weathering due to the flooding of these areas could substantially reduce the global weathering effect, thus weakening the negative feedback on global warming. It is also noted that the extensive warming could bring about a decrease in ice sheet area, especially in Greenland, which would open up some potentially very active weathering regions [Kump and Alley, 1994]. However, the extent of this areal reduction of ice sheet cover over a few thousand years is likely to be overwhelmingly compensated by the area of land flooded by sea level rise.

Another factor of some relevance is the interaction with land biogeochemistry. There has been an extensive discussion in recent years on the role of mid- to high-latitude peatlands in the context of a rapidly warming Earth, especially with regards to the decarbonation of these ecosystems and subsequent release of greenhouse gases in the atmosphere that could greatly amplify global warming. While the release of methane by itself does not directly affect terrestrial weathering, there are a variety of soil processes within peatlands which are triggered or amplified by warming and these would have a significant local effect on the chemical dissociation of rocks.

There are many other factors which would be worth investigating. For example, a distinction between physical and chemical weathering would allow the inclusion of factors such as altitude, which is important because wind and relief/slope play a major role in physical weathering. The impact of ground frost at higher latitudes also leads to erosion, and this could increase weathering rates in colder climates. Finally, one cannot ignore anthropological impacts, in particular the spread of modern agriculture, in which crop yields are often boosted using mineral fertilisers and other chemicals, which mix in with the soil water and accelerates the erosion of the bedrock. Other features of the Anthropocene worth mentioning include acid rain and land use change, all of which need to be taken into consideration in order to better represent the modern dynamics of global biogeochemistry. Unfortunately, it is unlikely that most of these factors can be properly integrated in current low- and intermediate-complexity climate models, on account of them requiring a spatial resolution much finer than what most EMICs can offer. For example, the UVic model's $1.8^{\circ} \times 3.6^{\circ}$ resolution cannot resolve physical mechanisms which occur over a single-kilometer spatial scale.

There is the potential for a spatially-explicit weathering scheme to be useful in other contexts as well. For example, *Mysak* [2008] examined various scenarios for the beginning of the next ice age, but concluded that the event was likely to be delayed by at least several 10^4 years, and perhaps indefinitely, in light of current anthropogenic carbon emissions. However, some would argue [*Archer*, 2005] that the presence of an interactive carbon cycle may render the next ice age unavoidable, as the legacy of anthropogenic activity is more forcefully removed from the atmosphere-ocean system. Our two-dimensional scheme might also be used to provide a better quantitative assessment rock weathering changes during glacial inceptions and deglaciations. There is still a considerable uncertainty surrounding the role of weathering during glacial cycles, as it is unclear at this point whether the loss of high-latitude land to ice sheets would have been compensated by the emergence of continental shelves due to retreating sea levels. Should the latter prove to have had a greater influence on weathering rates over the former, rock weathering would have acted as a positive, rather than negative, feedback mechanism on global climate change, which is a surprising outcome.

Another time period worth investigating would be the Paleocene-Eocene Thermal Maximum (PETM), which is a geologically brief period of intense warming at the Paleocene-Eocene boundary caused by a massive release of 13-C rich carbon. While the possible causes of the carbon excursion are well known, it has been proposed that the termination of the PETM – several 10^5 years after its inception – may have been brought about by an increase in global weathering rates. More generally, the rock weathering negative feedback mechanism has often been cited [*Walker et al.*, 1981] as the main cause of the gradually receding atmospheric CO₂ levels during the Phanerozoic, and especially during the current Cenozoic, and one of the main causes behind the icehouse climate which the Earth is experiencing since the onset of Antarctic glaciation 30 million years ago.

This work has established the importance of using a spatially-explicit weathering scheme to better represent long-term changes in carbon biogeochemistry. Our approach, although crude, has demonstrated that weathering can be integrated on the grid-cell level and still produce reasonable results. This study did not take into account the more subtle aspects of spatial variability, such as the impacts of ice sheets, sea level changes, and local factors such as soil activity and topography. These are therefore important processes to include in future analyses of the effect of deglacial weathering changes on ocean biogeochemistry and climate change.

References

Amiotte Suchet, P. and Probst, J. L. (1995): A global model for present day atmospheric/soil CO₂ consumption by chemical erosion of continental rocks (GEM-CO₂). *Tellus B*, 47, 273-280.

Amiotte Suchet, P., Probst, J. L., and Ludwig, W. (2003): Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO₂ uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochem. Cycles*, 17, 1038-1051.

Archer, D. (1996): A data-driven model of the global calcite lysocline. *Global Biogeochem*. *Cycles*, 10, 511-526.

Archer, D. (2005): Fate of fossil fuel CO₂ in geologic time. J. Geophys. Res. (Oceans), 110, 9-14.

Archer, D., and Brovkin, V. (2008): The millennial atmospheric lifetime of anthropogenic CO₂. *Clim. Change*, 90, 283-297.

Archer, D., Kheshgi, H., and maier-Reimer, E. (1997): Multiple timescales for neutralization of fossil fuel CO₂. *Geophys. Res. Lett.*, 24, 405-408.

Archer, D., Kheshgi, H., and Maier-Reimer, E. (1998): Dynamics of fossil fuel CO₂ neutralization by marine CaCO₃. *Global Biogeochem. Cycles*, 12, 259-273.

Archer, D., Eby, M., Brovkin, V., et al. (2009): Atmospheric lifetime of fossil fuel carbon dioxide. *Annu. Rev. Earth Planet. Sci.*, 37, 117-134.

Berger, A. L. (1978): Long-term variations of daily insolation and Quaternary climatic changes. *J. Atmos. Sci.*, 35, 2362-2368.

Bergman, N. M., Lenton, T. M., and Watson, A. J. (2004): COPSE: A new model of biogeochemical cycling over phanerozoic time. *Am. J. Sci.*, 304, 397-437.

Berner, R. A. (1990): Atmospheric carbon dioxide levels over Phanerozoic time. *Science*, 249, 1382-1386.

Berner, R. A. (1991): A model for atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.*, 291, 339-376.

Berner, R. A. (1994): GEOCARB II: A revised model of atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.*, 294, 56-91.

Berner, R. A. (1998): The carbon cycle and carbon dioxide over Phanerozoic time: the role of land plants. *Phil. Trans. R. Soc. Lond. B*, 353, 75-82.

Berner, R. A., and Kothavala, Z. (2001): GEOCARB III: A revised model of atmospheric CO₂ over Phanerozoic time. *Am. J. Sci.*, 301, 182-204.

Berner, R. A., Lasaga, A. C., and Garrels, R. M. (1983): The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.*, 283, 641-683.

Bitz, C. M., Holland, M. M., Weaver, A., J., and Eby, M. (2001): Simulation the ice-thickness distribution in a coupled climate model. *J. Geophys. Res.*, 106, 2441-2463.

Bluth, G. J. S., and Kump, L. R. (1994): Lithologic and climatologic controls of river chemistry. *Geochim Cosmochim. Acta*, 58, 2341-2359.

Brault, M.-O., Mysak, L. A., and Matthews, H. D. (2016): Carbon-cycle implications of terrestrial weathering changes since the Last Glacial Maximum. *FACETS*

Brovkin, V., Ganopolski, A., Archer, D., and Munhoven, G. (2012): Glacial CO₂ cycle as a succession of key physical and biogeochemical processes. *Clim. Past.*, 8, 251-264.

Caldeira, K. (2006): Forests, climate, and silicate rock weathering. J. Geochem. Expl., 88, 419-422.

Cao, L., Bala, G., Caldeira, K., Nemani, R. and Ban-Weiss, G. (2010): Importance of carbon dioxide physiological forcing to future climate change. *Proc. Nat. Acad. Sci.*, 107, 9513-9518.

Clark, P. U., Shakun, J. D., Marcott, S. A., et al. (2016): Consequences of twenty-first-century policy for multi-millennial climate and sea-level change. *Nature Climate Change*, doi: 10.1038.

Colbourn, G., Ridgwell, A. and Lenton, T. M. (2013): The Rock Geochemical Model (RokGeM) v0.9. *Geosci. Model Dev.*, 6, 1543-1573.

Colbourn, G., Ridgwell, A., and Lenton, T. M. (2015): The time scale of the silicate weathering negative feedback on atmospheric CO₂. *Glob. Biogeochem. Cycles*, 29, 583-596.

Cox, P. (2001): Description of the "TRIFFID" Dynamic Global Vegetation Model. *Met Office*: Hadley Centre technical note 24.

Cox, P., Betts, M., Bunton, R. A., Essery, C. B., Rowntree, R. L., and Smith, J. (1999): The impact of new land surface physics on the GCM simulation of climate and climate sentisivity. *Clim. Dyn.*, 15, 183-203.

Donnadieu, Y., Goddéris, Y., and Bouttes, N. (2009): Exploring the climatic impact of the continental vegetation on the Mezosoic atmospheric CO₂ and climate history. *Clim. Past*, 5, 85-96.

Doughty, C. E., Wolf, A., & Field, C. B. (2010): Biophysical feedbacks between the Pleistocene megafauna extinction and climate: The first human - induced global warming? *Geophys. Res. Lett.*, 37, L15703.

Ebelmen, J. J. (1845): Sur les produits de la décomposition des espèces minérales de la famille des silicates. *Ann. Mines*, 7, 3-66.

Eby, M., Zickfeld, K., Montenegro, A., et al. (2009): Lifetime of anthropogenic climate change: Millennial time scales of potential CO₂ and surface temperature perturbations. *J. Clim.*, 22, 2501-2511.

Ewen, T. L., Weaver, A. J., and Eby, M. (2004): Sensitivity of the inorganic ocean carbon cycle to future climate warming in the UVic coupled model. *Atmos. Ocean*, 42, 23-42.

Fanning, A. F., and Weaver, A. J. (1996): An atmospheric energy-moisture balance model: climatology, interpentadal climate change and coupling to an ocean general circulation model. *J. Geophys. Res*, 128, 15111-15128.

Foster, G. L., and Vance, D. (2006): Negligible glacial-interglacial variation in continental chemical weathering rates. *Nature*, 444, 918-921.

Gaillardet, J., Dupré, B., Louvat, P., and Allègre, C. J. (1999): Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. *Chem. Geol.*, 159, 3-30.

Gibbs, M. T., and Kump, L. R. (1994): Global chemical erosion during the last glacial maximum and the present: Sensitivity to changes in lithology and hydrology. *Paleoceanography*, 9, 529-543.

Gibbs, M. T., Bluth, G. J. S., Fawcett, P. J., and Kump, L. R. (1999): Global chemical erosion over the last 250Myr; variations due to changes in paleogeography, paleoclimate, and paleogeology. *Am. J. Sci.*, 299, 611-651.

Goddéris, Y., François, L.M., Probst, A., et al. (2006): Modelling weathering processes at the catchment scale: The WITCH numerical model. *Geochimica et Cosmochimica Acta*, 70, 1128-1147.

Harmon, R. S., White, W. B., Drake, J. J., and Hess, J. W. (1975): Regional hydrochemistry of North American carbonate terrains. *Water Resour. Res.*, 11, 963-967.

Hartmann, J., Jansen, N., Dürr, H. H., Kempe, S., and Köhler, P. (2009): Global CO₂consumption by chemical weathering: What is the contribution of highly active weathering regions? *Global and Planet. Change*, 69, 185-194.

Hays, J. D., Imbrie, J., & Shackleton, N. J. (1976): Variations in the Earth's Orbit: Pacemaker of the Ice Ages. *Science*, 194, 1121-1132.

Imbrie, J., & Imbrie, J. Z. (1980) : Modeling the climatic response to orbital variations. *Science*, 207, 943-953.

Indermühle, A., Stocket, T. F., Joos., F., Fischer, H., Smith, H., Wahlen, M., Deck, B., Mastroianni, D., Tschumi, J., Blunier, T., Meyer, R., and Stauffer, B. (1999): Holocene carboncycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica. *Nature*, 398, 121-126.

Kalnay, E., et al. (1996): The NCEP/NCAR 40-year reanalysis project, *Bull. Am. Meteorol. Soc.*, 77, 437-471.

Kump, L. R., & Alley, R. B. (1994): Global chemical weathering on glacial time scales. (P. of National Research Council, Ed.) *Material Fluxes on the Surface of the Earth*, pp. 46-60.

Kump, L. R., & Arthur, M. A. (1997). Global chemical erosion during the Cenozoic: Weatherability balances the budget. (W. Ruddiman, Ed.) *Tectonic Uplift and Climate Change*, pp. 399-426.

Kump, L. R., Brantley, S. L., & Arthur, M. A. (2000): Chemical weathering, atmospheric CO₂, and climate. *Annu. Rev. Earth Planet. Sci.*, 28, 611-667.

Lagache, M. (1979): New data on the kinetics of the dissolution of alkali feldspars at 200 C in CO₂ charged water. *Geochim. Cosmochim. Acta*, 40, 157-161.

Lenton, T. M, and Britton, C. (2006): Enhanced carbonate and silicate weathering accelerates recovery from fossil fuel CO₂ perturbations, *Global Biogeochem. Cycles*, 20, GB3009.

Ludwig, W., Amiotte-Suchet, P., and Probst, J.-L. (1999): Enhanced chemical weathering of rocks during the last glacial maximum: a sink for atmospheric CO₂? *Chem. Geol.*, 159, 147-161.

Matthews, H. D., and Caldeira, K. (2008): Stabilizing climate requires near-zero emissions. *Geophys. Res. Lett.*, 35, L04705.

Matthews, H. D., Weaver, A. J., and Meissner, K. J. (2005): Terrestrial carbon cycle dynamics under recent and future climate change. *J. Clim.*, 18, 1609-1628.

Matthews, H. D., Eby, M., Ewen, T., Friedlingstein, P. and Hawkins, B. J. (2007): What determines the magnitude of carbon cycle-climate feedbacks?. *Global Biogeochemical Cycles*, 21, GB2012.

Meissner, K. J., Weaver, A. J., Matthews, H. D., and Cox, P. (2003): The role of land surface dynamics in glacial inception: A study with the UVic Earth System Climate Model, *Clim. Dyn.*, 21, 515-537.

Meissner, K. J., McNeil, B. I., Eby, M., and Wiebe, E. C. (2012): The importance of the terrestrial weathering feedback for multimillennial coral reef habitat recovery. *Global Biogeochem. Cycles*, 26, GB3017.

Meybeck, M. (1987): Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am. J. Sci.*, 287, 401-428.

Milankovitch, M. (1941): Kanon der Erdbestrahlung und seine Andwendung auf das Eiszeitenproblem. Belgrade: R. Serbian Acad.

Mills, B., Daines, S. J., and Lenton, T. M. (2014): Changing tectonic controls on the long-term carbon cycle from Mesozoic to present. *Geochem. Geophys. Geosyst.*, 15, 4866-4884.

Moon, S., Chamberlain, C. P., and Hilley, G. E. (2014): New estimates of silicate weathering rates and their uncertainties in global rivers. *Geochim Cosmochim Acta*, 134, 257-274.

Montenegro, A., Brovkin, V., Eby, M., Archer, D., and Weaver, A. J. (2007): Long term fate of anthropogenic carbon. *Geophys. Res. Lett.*, 34, 19707-19711.

Munhoven, G. (2002): Glacial-interglacial changes of continental weathering: estimates of the related CO_2 and HCO_3^- flux variations and their uncertainties. *Global Planet. Change*, 33, 155-176.

Nugent, K. A. and Matthews, H. D. (2012): Drivers of future northern latitude runoff change. *Atmosphere-Ocean*, 50, 197-206.

Pacanowski, R. C. (1995): MOM 2 documentation, user's guide and reference manual. Princeton: GFDL Ocean Group Technical Report, NOAA, GFDL. 232pp.

Peltier, W. R. (2004): Global glacial isostasy and the surface of the ice-age Earth: The ICE-5G (VM2) Model and GRACE. *Annu. Rev. Earth. Planet. Sci.*, 32, 111-149.

Raymo, M. E., Ruddiman, W. F., & Froelich, P. N. (1988): Influence of late Cenozoic mountain building on ocean geochemical cycles. *Geology*, 16, 649-653.

Ridgwell, A., and Hargreaves, J. C. (2007): Regulation of atmospheric CO₂ by deep-sea sediments in an Earth system model. *Global Biogeochem. Cycles*, 21, GB2008-2021.

Ridgwell, A., and Zeebe, R. (2005): The role of the global carbonate cycle in the regulation and evolution of the Earth system. *Earth Plan. Sc. Lett.*, 234, 299-315.

Ridgwell, A., Zondervan, J. C., Hargreaves, J. C., Bijma, J., & Lenton, T. M. (2007): Assessing the potential long-term increase of oceanic fossil fuel CO₂ uptake due to CO₂-calcification feedback. *Biogeosciences*, 4, 481-492.

Ruddiman, W. F. (2003): The Anthropogenic Greenhouse Era Began Thousands of Years Ago. *Clim. Change*, 61, 261-293.

Ruddiman, W. F. (2006): Orbital changes and climate. Quat. Sci. Rev., 25, 3092-3112.

Ruddiman, W. F. (2008): *Earth's Climate: Past and Future* (2nd ed.). New York: W. H. Freeman and Company.

Sarmiento, J., & Gruber, N. (2006): Ocean Biogeochemical Dynamics. Princeton University Press.

Schartau, M., and Oschlies, A. (2003): Simultaneous data-based optimization of a 1d-ecosystem model at three locations in the North Atlantic: I. Mothod and parameter estimates. *Journal of Marine Research*, 61, 765-793.

Schmittner, A., Oschlies, A., Matthews, H. D., and Galbraith, E. D. (2008): Future changes in climate, ocean circulation, ecosystems, and biogeochemical cycling simulated for a business-as-usual CO₂ emission scenario until year 4000 AD. *Global Biogeochem. Cycles*, 22, GB1013.

Schott, J., Oelkers, E. H., Bénézeth, P., Goddéris, Y., & François, L. (2012): Can accurate kinetic laws be created to describe chemical weathering? *C. R. Geosciences*, 344, 568-585.

Simmons, C. T., Matthews, H. D., and Mysak, L. A. (2016): Deglacial climate, carbon cycle and ocean chemistry changes in response to a terrestrial carbon release. *Clim. Dyn.*, 46, 1287-1299.

Sundquist, E. (1991): Steady- and non-steady-state carbonate-silicate controls on atmospheric CO₂. *Quaternary Sci. Rev.*, 10, 283-296.

Taylor, L.L., Quirk, J., Thorley, R.M., et al. (2015): Enhanced weathering strategies for stabilizing climate and averting ocean acidification. *Nature Climate Change*, 6, 402-406.

Uchikawa, J., and Zeebe, R. E. (2008): Influence of terrestrial weathering on ocean acidification and the next glacial inception. *Geophys. Res. Lett.*, 35, L23608.

Urey, H. C. (1952): *The planets: their origin and development*. New Haven, Conn: Yale Univ. Press.

Valdes, P. J., Beerling, D. J., & Johnson, C. E. (2005): The ice age methane budget. Geophys. Res. Lett., 32, L02704.

Walker, J. C., and Kasting, J. F. (1992): Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 97, 151-189.

Walker, J. C., Hays, P. B., & Kasting, J. F. (1981): A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *J. Geophys. Res.*, 86, 9776-9782.

Weaver, A. J., et al. (2001): The UVic Earth System Climate Model: model description, climatology, and applications to past, present and future climates. *Atmos. Ocean*, 39, 361-428.

Yin, Q. Z., and Berger, A. (2012): Individual contribution of insolation and CO_2 to the interglacial climates of the past 800,000 years. *Clim. Dyn.* 38, 709-724.

Zachos, J. C., Dickens, G. R., & Zeebe, R. E. (2008). An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics. *Nature*, 451, 279-283.

Zachos, J. C., Röhl, U., Schellenberg, S. A., Sluijs, A., Hodell, D. A., Kelly, D. C., . . . Kroon, D. (2005): Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science*, 308, 1611-1615.

Zeebe, R. E., & Caldeira, K. (2008): Close mass balance of long-term carbon fluxes fron ice-core CO₂ and ocean chemistry records. *Nature geosci.*, 1, 312-315.