

FACULTY OF GEOSCIENCES

How climate change will affect the influence of silicate weathering on atmospheric CO₂

Bachelor thesis

Lora Strack van Schijndel

29-06-2017



Utrecht University

How climate change will affect the influence of silicate weathering on atmospheric CO₂

State of the art review

Author: Lora Strack van Schijndel (3968006)

Supervisor: Mara Baudena

29-06-2017

Bachelor thesis environmental sciences

Abstract

Human induced greenhouse gas emissions cause an increase in global mean surface temperature. Silicate weathering is seen as the most important factor in stabilizing climate over geological time scales. Important factors in the development of the effect of silicate weathering on atmospheric carbon dioxide are thought to be temperature, runoff, vegetation, tectonic activity, lithology and processes affecting calcium carbonate burial rates and formation. Increasing temperature, runoff and vegetation due to global warming are expected to enhance silicate weathering and this might lead to reduced atmospheric carbon dioxide levels to nearly pre-industrial over hundreds and thousands years. However, many uncertainties about this process are present, especially in the effects of tectonic activity, vegetation, land use changes and the adaptive response of calcifying organisms.

Samenvatting

Antropogene broeikasgastuitstoot veroorzaakt een stijging in de gemiddelde oppervlaktetemperatuur op globale schaal. Silicaatverwerking wordt gezien als de belangrijkste factor in de stabilisatie van het klimaat over geologische tijdschalen. Belangrijke factoren die de invloed van silicaatverwerking op de atmosferische koolstofdioxide bepalen zijn vermoedelijk temperatuur, waterafvloeiing, vegetatie, tektonische activiteit, lithologie en processen die de sedimentatiesnelheid van calciumcarbonaat beïnvloeden. Het is aannemelijk dat stijgingen in temperatuur, waterafvloeiing en vegetatie veroorzaakt door de opwarming van de aarde zullen leiden tot versterkte silicaatverwerking. In honderdduizenden jaren leidt dit mogelijk tot verminderde atmosferische koolstofdioxidegehalten tot nabij pre-industriële waarden. Echter, er bestaan verschillende onzekerheden over het verloop van dit proces. Deze onzekerheden zitten vooral in de effecten van tektonische activiteit, vegetatie, veranderingen in landgebruik en de adaptieve respons van kalkvormende organismen.

Contents

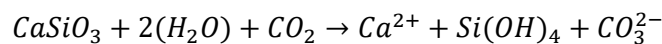
Contents	2
Introduction	3
Chapter 1: Influence of climate related factors on silicate weathering rates.....	6
1.1 Temperature and runoff.....	6
1.2 Vegetation	7
Chapter 2: Climate independent factors	9
2.1 Lithology.....	9
2.2 Tectonic uplift.....	9
Chapter 3: Limitation.....	10
Chapter 4: CaCO ₃ burial.....	11
4.1 Acidification.....	11
4.2 Reduction of the AMOC.....	11
Chapter 5: In a changing climate	12
5.1 In past climates.....	12
5.2 In our future climate.....	14
Conclusion	18
Bibliography.....	19

Introduction

Several changes in the climate system are observed since the 1950s, and these are very likely to have been induced by humans (IPCC, 2013). The concentrations of greenhouse gases have increased, the atmosphere and ocean have warmed, there is less snow and ice and the sea level has risen (IPCC, 2014). About three-quarter of the anthropogenic greenhouse gas emissions consists of carbon dioxide (CO₂) and this makes CO₂ the largest contributor to the temperature rise (IPCC, 2013). Since the year 1870 already 1900 gigatons (Gt) of CO₂ from anthropogenic resources was emitted by the year 2011 and to limit human-induced warming to less than 2°C these emissions should be kept below about 2900 GtCO₂.

It is not the first time the earth deals with a rapid CO₂ rise. For instance during the Paleocene-Eocene Thermal Maximum (PETM, ca. 56 Ma), thousands GtCO₂ had been emitted in several thousands of years (Penman, 2016). On geological timescales, this is seen as a rapid rise (Kump, Bralower, & Ridgwell, 2009; Penman, 2016; Zachos et al., 2005). An important process which has played a crucial role in the termination of this event is silicate weathering. The accelerated chemical weathering of terrestrial silicate rocks resulted in the extraction of CO₂ from the atmosphere. Elevated atmospheric CO₂ concentrations result in surface warming and thus intensification of the hydrologic cycle. Increased temperature and increased precipitation are thought to be key factors in the acceleration of weathering of terrestrial silicate rocks (Penman, 2016). Since the silicate weathering process results in intensified CO₂ consumption in a warmer climate, silicate weathering is seen as an important factor in stabilizing climate and maintaining habitable temperatures on Earth (Berner, Lasaga, & Garrels, 1983). On geological time scales, weathering of silicate minerals on the continents accounts for the largest sink of atmospheric CO₂ (Wallmann, 2001).

An example of a silicate weathering reaction is the reaction of the calcium silicate mineral wollastonite (CaSiO₃) (De La Rocha & Conley, 2017):



Silicate weathering releases silica to solution and it converts CO₂ into a bit of carbonate alkalinity in the form of carbonate (CO₃²⁻) or bicarbonate (HCO₃⁻). Carbonate alkalinity can be written down as (Archer, 2010):

$$alk_c = [HCO_3^-] + 2[CO_3^{2-}]$$

These CO₃²⁻ and HCO₃⁻ ions have the capacity to consume free protons (H⁺) which lower the pH of the ocean. Therefore, alkalinity acts as a pH buffer preventing ocean acidification (Archer, 2010). By converting CO₂ into CO₃²⁻ or HCO₃⁻, silicate weathering reacts as a pH buffer for the oceans. Calcifying organisms like seashells or corals use part of the CO₃²⁻ ions released by silicate weathering to produce CaCO₃ (De La Rocha & Conley, 2017). A part of this CaCO₃ is dissolved in

the water column but another part is buried in ocean seafloor sediment and will thus be removed from the atmosphere-ocean system (see Figure 1) (Archer, Kheshgi, & Maier-Reimer, 1998).

Since the magnitude of silicate weathering rates is climate sensitive, the effects of silicate weathering may possibly act as a negative climate feedback in the future by buffering

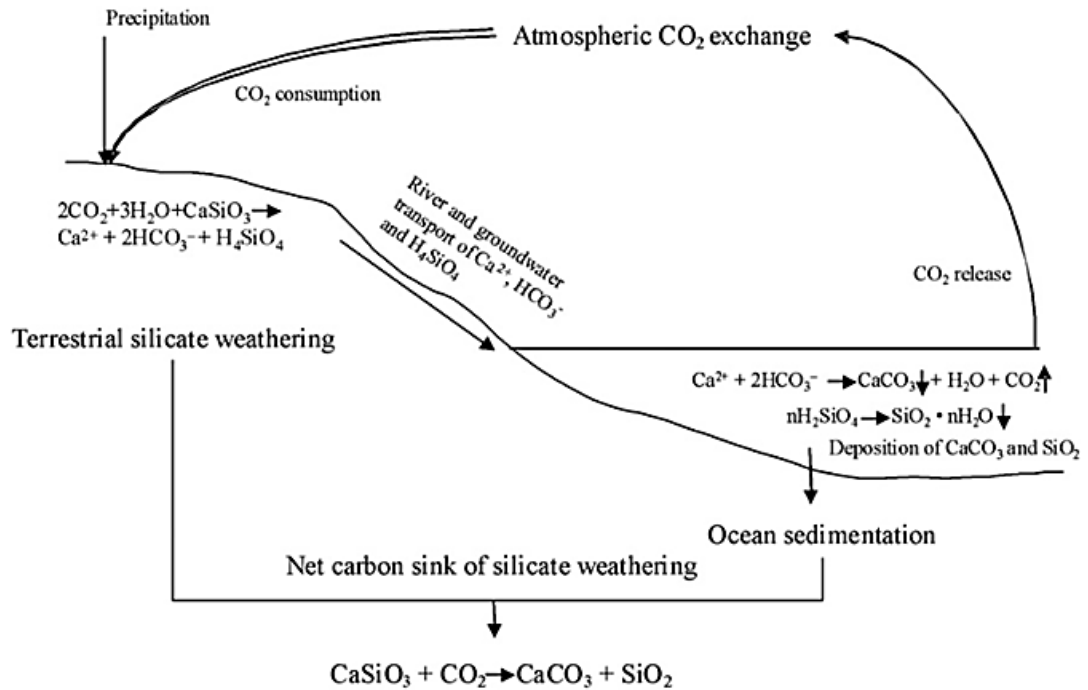


Figure 1: Major processes related to net atmospheric CO₂ consumption and Si release during silicate weathering (Song et al., 2012).

anthropogenic CO₂ emissions (Foster, Royer, & Lunt, 2017). Few modelling studies examined the effects of enhanced silicate weathering on future atmospheric CO₂ concentrations and surface temperature (Archer, 2005; Lenton & Britton, 2006). However, these studies often lack incorporation of important factors like for instance vegetation and land use decisions. Besides, the effects of isolated factors like temperature, runoff and plate tectonics are still under debate (Eiriksdottir, Gislason, & Oelkers, 2013; Riebe, Kirchner, Granger, & Finkel, 2001). Therefore, the research question of this thesis will be: *To what extent will changes in the future climate system influence directly or indirectly silicate weathering and its effects on atmospheric CO₂ concentrations?* The most important factors influencing the effect of silicate weathering on atmospheric CO₂ will be examined and therefore this review might be used as a theoretical background for modeling the effects of silicate weathering on future climate.

Silicate weathering in combination with CaCO₃ burial is a process that takes place in thousands of years (Harvey, 2000) and the effects of enhanced silicate weathering on atmospheric CO₂ will become visible over hundreds and thousands of years (Archer et al., 1998). Therefore this climate feedback is not relevant for the human population living on earth nowadays, although it is relevant for the way the earth's biochemical cycles will respond to anthropogenic global warming on longer timescales.

The most important climate related factors that are thought to have a positive influence on silicate weathering rates are temperature, runoff and vegetation. Tectonic activity and lithology are thought to be the most important climate independent factors influencing silicate weathering rates (Berner, 1995). Ocean acidification and reduction of the Atlantic Meridional Overturning Circulation (AMOC) are climate related factors that are thought to have a negative influence on the effects of silicate weathering on atmospheric CO₂. Anthropogenic addition of CO₂ to the climate system is causing acidification of the oceans (Ries, Cohen, & McCorkle, 2009). During ocean acidification, the CaCO₃ production is reduced and this leads to a decrease in CaCO₃ burial (Penman, 2016). Weakening of the AMOC due to climate change is expected to induce a decline in CaCO₃ export to ocean sediments as well (Chikamoto, Matsumoto, & Ridgwell, 2008; Tyrrell, 2011). The interaction between the different factors and the effect of silicate weathering on atmospheric CO₂ concentrations is shown in figure 2. How the climate related factors affect silicate weathering rates is discussed in the first chapter, followed by the effects of climate independent factors. After that it is explained how silicate weathering rates act within different limitation scenarios. Thereafter, the factors affecting CaCO₃ burial are discussed and at last the effects of silicate weathering on atmospheric CO₂ in a changing climate are examined.

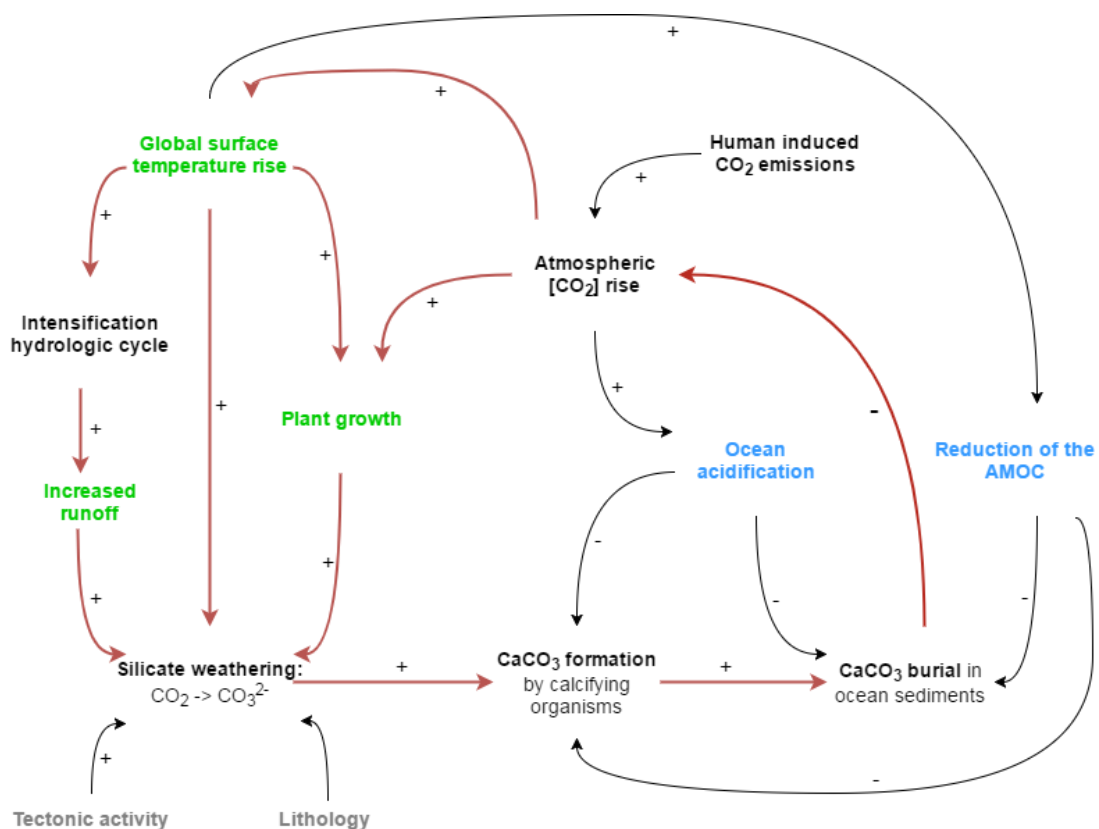


Figure 2: How the factors and processes incorporated in silicate weathering and CaCO₃ burial are related, represented in a conceptual model. The green factors represent the climate related factors and the grey factors the climate independent factors affecting silicate weathering rates. The blue factors are related to CaCO₃ burial. The red arrows represent the relationships incorporated in the climate feedback process.

Chapter 1: Influence of climate related factors on silicate weathering rates

1.1 Temperature and runoff

Temperature tends to have a strong positive influence on silicate weathering rates (Berner et al., 1983; Walker, Hays, & Kasting, 1981). It is argued that temperature is the main factor controlling silicate weathering (Walker et al., 1981), but there is no consensus about this statement (Raymo & Ruddiman, 1992; Riebe et al., 2001). An increase in temperature accelerates the weathering reaction because it activates energy effects on mineral dissolution kinetics (Banwart, Berg, & Beerling, 2009). However, this process is poorly understood and therefore it is difficult to predict the effects of changing temperature on silicate weathering rates (Pogge von Strandmann et al., 2017). Especially in laboratory environments the dependence of silicate weathering rates on temperature seems to be strong, however in the field this dependency is diminished due to the effects of other environmental factors (Kump, Brantley, & Arthur, 2000). It is hard to isolate the effect of temperature from other factors like precipitation, geomorphology, vegetation and lithology, especially if the scale of the research area increases (White et al., 1999).

In general higher temperatures lead to higher silicate weathering rates, however this is not applicable for every environment. For example in extremely hot environments the weathering rates seem to be extremely low and low runoff rates can partly cancel the positive influence of temperature on silicate weathering (West, Galy, & Bickle, 2005). For instance in the Nsimi humid tropic watersheds the mean annual temperature is relatively high (24°C), but the silicate weathering rates are low. This is expected to be caused by the relatively high water table and low runoff (Braun et al., 2005). For the large rivers on a global scale no significant correlation is found between temperature and silicate weathering rates (Gaillardet, Dupré, Louvat, & Allègre, 1999). However, if rivers with exceptional low weathering rates due to lack of runoff are excluded, weathering rates increase about 5 times every 5°C (Gaillardet et al., 1999). This confirms the positive relationship between runoff and temperature. Another possible reason why temperature effects in large-scale river systems are failed to detect is that the scale of the research area had been too large (White et al., 1999).

Runoff and precipitation are directly correlated (see Figure 3), although not the same for every environment (White & Blum, 1995). Generally higher runoff rates account for accelerated silicate weathering rates. Due to the large combined positive effect of temperature and runoff on silicate weathering, tropical regions play an important role in global silicate weathering fluxes. This suggests continental averages for temperature and precipitation are not representative for the calculation of global silicate weathering rates in climate models (White & Blum, 1995). Since both temperature and runoff are climate dependent factors and thus commonly co-vary, it is challenging to identify the isolated roles of these factors (Eiriksdottir et al., 2013). Once the effects of runoff are normalized, dissolution rates of common silicate minerals increase 2-10% for every degree of temperature increase, according to both experimental and natural studies (Pogge von Strandmann et al., 2017). According to a study in NE Iceland river catchments, a 1% rise in

runoff produces a 1% increase in silicate weathering rates (Eiriksdottir et al., 2013). However, due to dilution effects this response is not linear, and thus if runoff increases the positive effect of runoff on silicate weathering decreases (Berner, 1995). The combined effect of temperature and runoff on silicate weathering rates is shown in figure 4.

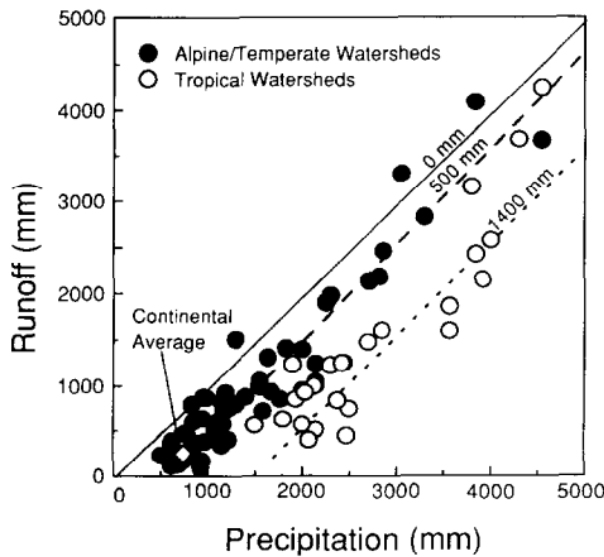


Figure 3: Correlation between watershed runoff and precipitation for alpine/temperate (filled dots) and tropical (open dots) watersheds (White & Blum, 1995).

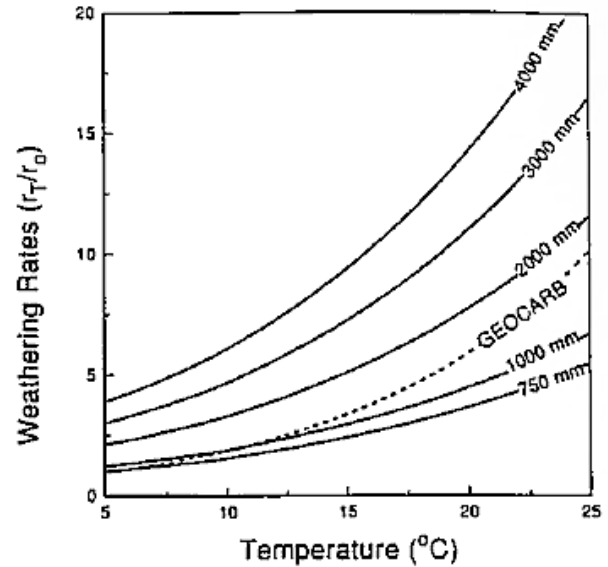


Figure 4: The observed relationship between silicate weathering rates and mean annual temperature and precipitation (White & Blum, 1995).

1.2 Vegetation

Another climate related factor that might have a large influence on silicate weathering rates is vegetation (Berner & Berner, 1997). The combination of high temperatures and vegetation has a strong positive effect on the rates of silicate weathering (Berner & Berner, 1997). Plants and the associated soil microbiota have a positive influence on silicate weathering rates in several ways. Plant rootlets generate organic acids during the uptake of nutrient elements from silicate minerals as well as during the decay of organic matter (Moulton, 1998). These organic acids lower soil pH what accelerates silicate weathering by attacking primary minerals. Excretion of CO_2 in the soil by plants results in lowering of soil pH as well (Drever, 1994). Another way plants accelerate silicate weathering rates is by their influence on hydrologic processes. Plants increase the recirculation of water by evapotranspiration and they prevent clay-rich soil from erosion (Moulton, 1998). This results in greater rainfall (Moulton, West, & Berner, 2000) and allows the weathering process to continue between rainfall events because the clay-rich soil captures water. The increase in rainfall replaces saturated solution with fresh solution and this might enhance weathering rates. Thereby, plant rootlets change soil porosity by fracturing the soil. This results in a more effective water flow around primary minerals (April & Keller, 1990). The influence of land plants on acidity of the soil is seen as a direct effect and the influence on the hydrologic cycle as an indirect effect on silicate weathering. Land plants might also affect silicate weathering rates by their influence on soil temperature. Decay of vegetation produces heat, while the forest

canopy results in soil cooling due to their shade (Moulton et al., 2000). Not all plant types have the same effect on silicate weathering rates. For instance bryophytes have a small effect on silicate weathering rates relative to vascular plants due to their small size and lack of a large root mass. Gymnosperms and angiosperms are also expected to have a different influence on silicate weathering rates due to differences in nutritional needs, growth rates and effects on soil chemistry (Moulton et al., 2000).

It is estimated that in basaltic areas where vegetation is present silicate weathering rates are 2-8 times as high as in bare rock surfaces (Song, Wang, Strong, Li, & Jiang, 2012), however the relative importance depends on plant type, climate and geology (Moulton et al., 2000). According to Drever (1994), the influence of land plants on silicate weathering appears to be relatively minor on a global scale. In local environments silicate weathering could be accelerated by up to a factor 10 due to the influence of land plants, but on a global scale this effect is probably no more than a factor 2 (Drever, 1994).

The influence of plants on silicate weathering is not taken into account in several studies on silicate weathering because it was initially thought that vegetation would not contribute to the output of silicate weathering in the long term due to a dynamic equilibrium (Song et al., 2012). For example in the research on the CO₂ consumption resulting from silicate weathering based on the 60 largest rivers of the world (Gaillardet et al., 1999) the impact of land plants is ignored. In more recent studies it is revealed that plants and soils significantly impact long-term biogeochemical cycles (Song et al., 2012). It is difficult to isolate the effects of vegetation on silicate weathering from the effects of other factors like temperature, runoff, lithology and tectonic activity (Moulton et al., 2000).

Chapter 2: Climate independent factors

2.1 Lithology

On a global scale silicate weathering accounts for 60% of the atmospheric CO₂ uptake and the remaining 40% is attributed to carbonate weathering (Amiotte Suchet, Probst, & Ludwig, 2003). Among the silicate rocks not all rock types have the same contribution to global CO₂ uptake. For example shales account for 40% of the CO₂ consumed on a global scale and almost 67% of the CO₂ consumed by silicate rocks while only 29% of the silicate rocks consists of shales (Amiotte Suchet et al., 2003). Sandstones are as abundant as shales but only consume 5% of the total atmospheric CO₂. Basalts account for 5% of the total atmospheric CO₂ as well, while only 5% of the continental area consists of basalts.

2.2 Tectonic uplift

Tectonic activity tends to play an important role in silicate weathering rates (Raymo & Ruddiman, 1992). Mountain uplift results in rugged relief under cold temperatures at high elevations. This rugged relief removes protective covers of weathered clay residues due to physical erosion and this allows greater exposure of primary silicate minerals and thus enhances silicate weathering. The cold temperatures induce greater physical weathering due to freeze-thaw and grinding caused by glaciers (Berner, 1995).

Recent studies suggest tectonic activity might be linked to climate as well (Bercovici & Ricard, 2014; Foley, Bercovici, & Landuyt, 2012). Cool climates are thought to promote tectonic activity because suppression of grain growth might weaken plate boundaries. Besides, cooler surface temperatures increase mantle convective stresses causing the convective forces to exceed the lithosphere's intrinsic strength more easily (Lenardic, Jellinek, & Moresi, 2008). In contrast warmer surface temperatures might lead to stronger lithospheric shear zones due to rapid grain growth causing a larger resistance to plate motions. If plate movement slows down due to higher surface temperature, lower CO₂ degassing rates occur (Foley, 2015). This lower degassing rate in combination with higher silicate weathering rates due to an increase in temperature and runoff might help buffering the earth's temperature. According to Foley (2015) the influence of climate on silicate weathering directly is far larger than the influence of climate on plate tectonics.

Chapter 3: Limitation

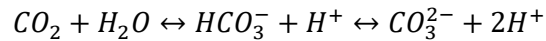
Multiple studies conclude that climate related factors are decisive for silicate weathering rates (Broecker & Sanyal, 1998; Gwiazda & Broecker, 1994; Walker et al., 1981). However, few studies argue that plate tectonics are the most important factor controlling silicate weathering rates (Raymo & Ruddiman, 1992; Riebe et al., 2001). A solution for this contradiction is to make a distinction between supply limited and kinetically limited silicate weathering (West et al., 2005). In the case of supply limitation, silicate weathering is limited by the supply of fresh rock at the surface and thus by physical erosion. If kinetics are limiting, silicate weathering is limited by temperature or runoff. Plate tectonics have a large influence on silicate weathering rates in a supply limited environment (Foley, 2015) and climate related conditions only have influence on silicate weathering rates if the area is kinetically limited (West et al., 2005). For example at lower erosion rates due to little tectonic activity increased temperature has a small effect on silicate weathering rates. If the erosion rates are higher, climate related factors like temperature limit weathering rates and thus have a relatively high influence (West et al., 2005).

Whether an area is supply or kinetically limited might also play a role in the influence of vegetation on silicate weathering rates. Vegetation is expected to merely have a positive influence on silicate weathering if the process is kinetically limited (Drever, 1994). Since land plants decrease physical erosion rates, vegetation might even decrease silicate weathering rates in a supply limited environment. Environments that were initially kinetically limited might become supply limited in the presence of vegetation. This transition possibly results in lower weathering rates.

Chapter 4: CaCO₃ burial

4.1 Acidification

Ocean acidification accounts for reduced CaCO₃ burial, and this will occur in a higher CO₂ world. CO₂ acts as an acidifier of the oceans because the solution of CO₂ in water results in the release of one or more free H⁺ ions according to the following equilibrium (Tyrrell, 2011):



In the ocean most of the CO₂ is converted into HCO₃⁻, releasing one H⁺ ion and this lowers the oceans pH (Tyrrell, 2011). A lower ocean pH leads to a decrease in CaCO₃ burial because it suppresses calcifying rates. In a relatively acid ocean, a larger amount of CO₃²⁻ ions is converted into HCO₃⁻ to buffer the pH. This leads to a decrease in CO₃²⁻ ions in the oceans. These CO₃²⁻ ions are used to form CaCO₃ and thus a decrease in CO₃²⁻ ions makes it harder for calcifying organisms to build their calcareous shells. Calcification rates are often directly influenced by pH as well, however this relationship is species dependent (Iglesias-Rodriguez et al., 2008).

4.2 Reduction of the AMOC

Another negative effect on CaCO₃ burial is the prospected decline of the AMOC. Warm high saline surface water flows to the North Atlantic where the high saline water cools and sinks due to its high density (Kuhlbrodt et al., 2007). This deep-water formation in the North Atlantic is seen as the main driver of the AMOC. Higher atmospheric CO₂ concentrations lead to warming of the upper layer of the oceans, making the surface water more buoyant compared with deeper waters. Addition of low saline water in high latitudes due to ice melting cause a decrease in density of the North Atlantic water because low saline water has a lower density than high saline water (Tyrrell, 2011). Warming of the surface water and addition of low saline water both lead to a decline in density of North Atlantic water and this diminishes deep water formation resulting in a decline of the AMOC. When the AMOC is reduced, less CO₃²⁻ is transported to the deep ocean and this enhances CaCO₃ dissolution in the sediments reducing the burial flux (Chikamoto et al., 2008). Thereby less nutrients are available in the surface water during a reduced AMOC because there will be less upwelling of high-nutrient deep water. This diminishes productivity of calcifying organisms and therefore less CaCO₃ is formed and transported to the deep ocean (Chikamoto et al., 2008).

Chapter 5: In a changing climate

5.1 In past climates

Although past climates are not direct analogues for the modern world, they might be seen as natural experiments to test the sensitivity of the ocean-climate system to changes in the carbon cycle (Holbourn, Kuhnt, Kochhann, Andersen, & Sebastian Meier, 2015). For instance during the PETM amounts of carbon similar to projected anthropogenic CO₂ emissions were released. This atmospheric CO₂ rise occurred in a timescale of 10³-10⁴ years, which is rapid relative to other CO₂ rises in the past (Penman, 2016). This CO₂ rise resulted in a temperature rise of about 5°C (Sluijs et al., 2006). The increase in atmospheric CO₂ during the PETM caused shallowing of the *lysocline* (Kelly, Nielsen, McCarren, Zachos, & Röhl, 2010). The lysocline refers to the transition depth from very low to high CaCO₃ dissolution rates (Sarmiento & Gruber, 2004). Beneath the lysocline CaCO₃ dissolution rates increase rapidly, and this depth is called the *calcite compensation depth* (CCD). Shallowing of the lysocline and the CCD diminishes the formation and burial of CaCO₃ (see Figure 5). According to carbon cycle models, enhanced silicate weathering neutralized ocean acidification resulting in deepening of the lysocline as the marine carbonate system recovered from the rapid CO₂ rise (See Figure 6). This recovery occurred after ~2000-3000 years. On geological time scales (10⁴-10⁶ years), the carbonate- silicate geochemical cycle driven by enhanced silicate weathering has played the largest role in the subduction of atmospheric CO₂. This process also has the largest potential for carbon sequestration (Kelly et al., 2010).

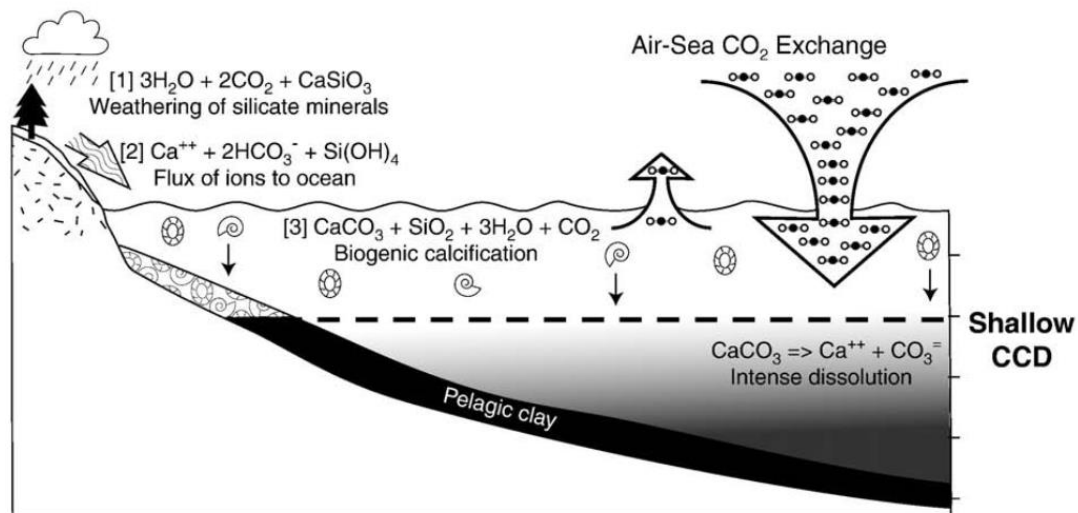


Figure 3: Schematic representation of carbon exchange between various reservoirs in the carbonate-silicate geochemical cycle. Rapid atmospheric CO₂ rise increases oceanic absorption of CO₂, causing the calcite compensation depth (CCD) to shoal. This reduces the burial flux of CaCO₃ (Kelly et al., 2010).

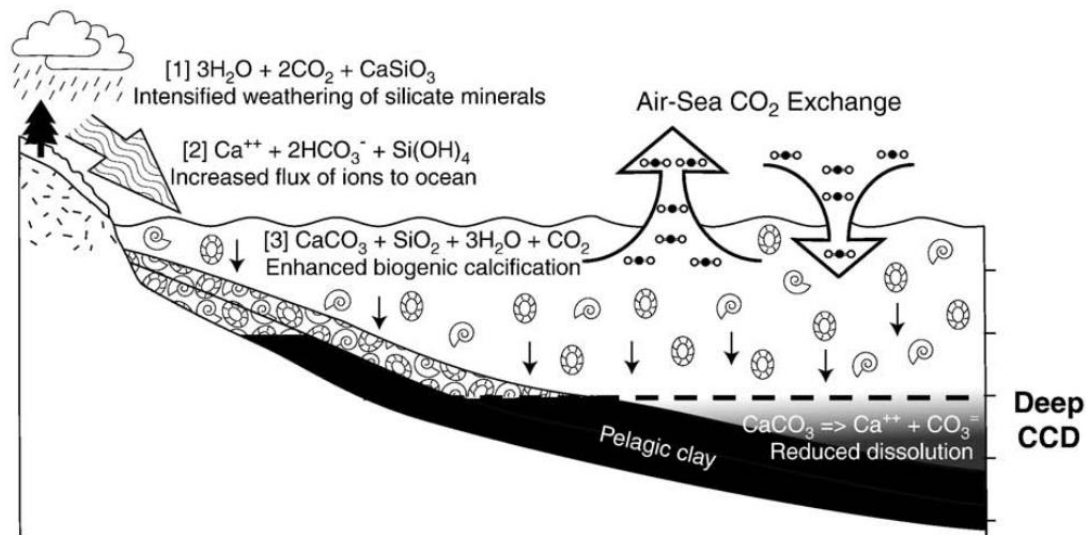


Figure 4: During the 'recovery phase' of the atmosphere-ocean system, accelerated silicate weathering rates result in the neutralization of ocean acidification and CCD deepening. The burial flux of CaCO_3 will strengthen due to the deepening of the CCD (Kelly et al., 2010).

Another phase of global warming has been the Miocene Climatic Optimum (MCO; ca. 17-14.7 Ma) (Holbourn et al., 2015). The exact values are still under debate, but atmospheric CO_2 is expected to have reached values of ~ 500 ppm during the MCO. By ca. 14-12 Ma, atmospheric CO_2 decreased to ~ 300 -200 ppm (Zhang, Pagani, Liu, Bohaty, & DeConto, 2013). This decrease supports a long-term coupling between climate and atmospheric CO_2 variations. The research done by Holbourn et al. (2015) supports the assumption that enhanced silicate weathering rates played a large role in this process.

Vegetation is also thought to have played an important role in silicate weathering rates in the past. The atmospheric CO_2 drop from the Early (~415 Ma) to the Late Devonian (~365 Ma) is expected to have been caused partly by the influence of the increase in height and complexity of vascular land plants on silicate weathering rates. During this period atmospheric CO_2 dropped from 6300 ppm to 2100 ppm. The largest part of this decrease is caused by the continental drift and an decrease of 1800 ppm is thought to be caused by the spreading of land plants on continental surfaces. The spreading of land plants resulted in rising surface temperatures due to a decreased albedo. This temperature rise promoted CO_2 consumption by silicate weathering (Le Hir et al., 2011).

During the breakup of the Pangea supercontinent (from 250 to 65 Ma), the paleogeographical setting tends to be the main factor controlling global climate (Donnadieu et al., 2006). The breakup of the supercontinent triggered an increase in continental runoff, resulting in enhanced silicate weathering. However, land plants might also have had a significant influence on silicate weathering rates during this period (Donnadieu, Godd ris, & Bouttes, 2009). In the research of Donnadieu et al. (2009) it is argued that the indirect effect of land plants on silicate weathering might have been as large as the direct effect.

It is expected that the AMOC also played a crucial role in silicate weathering rates in the past (Elsworth, Galbraith, Halverson, & Yang, 2017). During the Eocene-Oligocene boundary (33.7 Ma), intensification of the AMOC might have been an important factor in the rapid emplacement of the large ice sheet on Antarctica. Enhancement of the AMOC caused an increase of global surface air temperature over land by ~1%, resulting in a precipitation increase of ~5% over land. This change has influenced local climate patterns and caused enhanced silicate weathering. This intensified silicate weathering might explain the atmospheric CO₂ drawdown that is related to Antarctic ice sheet growth.

5.2 In our future climate

Variations in the magnitude of total solar irradiance (TSI) and changes in the atmospheric greenhouse gas content largely determined earth's climate on geological timescales. Nowadays a slow increase in TSI is going on, but a long-term decline in atmospheric CO₂ concentrations caused by enhanced silicate weathering neutralizes the effects of this increase almost completely. However, humanity's use of fossil fuels brings the atmospheric CO₂ to values not seen since 50 million years ago (Foster et al., 2017). If these values continue to rise in the coming centuries, there will be no geological precedent in the past half billion years for how the earth's geochemical cycle will respond.

Due to anthropogenic greenhouse gas emissions several changes in the climate system are going on that might affect silicate weathering rates and its related CaCO₃ burial. The atmospheric CO₂ concentration might rise from pre-industrial values of 280 ppm to 400- ~900 ppm in 2100 (IPCC, 2013). Due to this rise in atmospheric CO₂ concentrations the mean global surface temperature is prospected to have increased with ~2°C to ~4°C by the year 2100 with respect to the 1850-1950 values and might continue to rise in the following centuries (see Figure 7). The expected temperature rise will cause an increase in precipitation (see Figure 8). The temperature change will be highest in the polar regions and the precipitation change in the polar regions as well as in the equatorial region (IPCC, 2013). Since both temperature and precipitation have a positive influence on silicate weathering rates, enhanced silicate weathering is expected to buffer atmospheric CO₂ in the future. In hundreds and thousands of years, atmospheric CO₂ levels might be reduced to nearly pre-industrial levels (see Figure 9) (Lenton & Britton, 2006). However, these predictions are derived from highly simplified models.

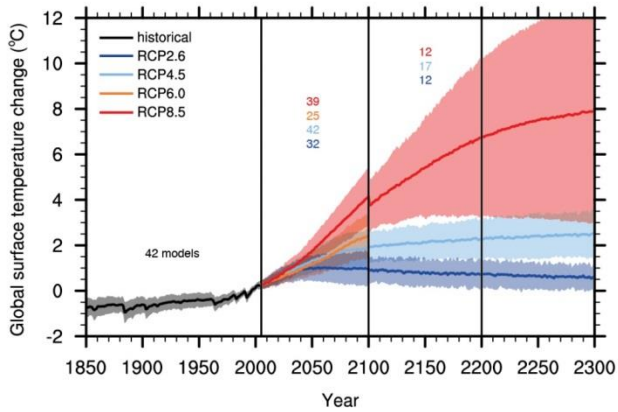


Figure 7: Expected global surface temperature rise for different climate scenarios (IPCC, 2013).

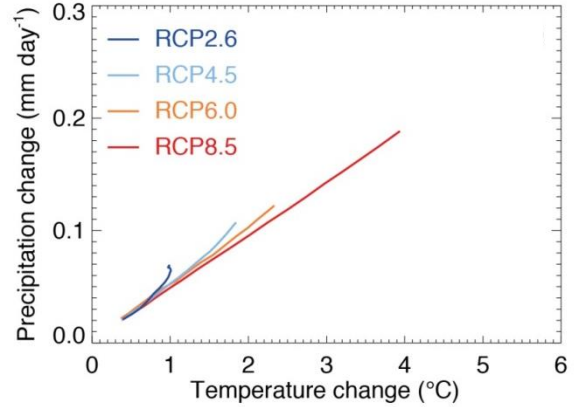


Figure 8: Expected increase in precipitation due to increased temperatures for different climate scenarios (IPCC, 2013).

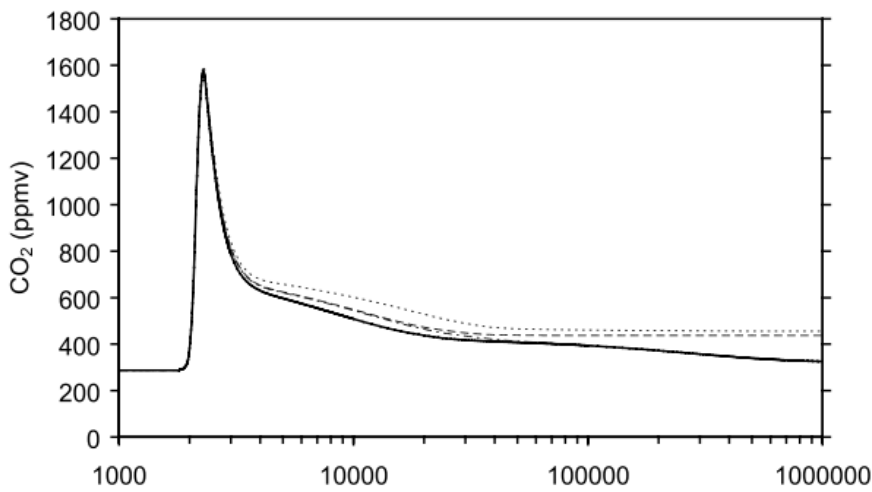


Figure 9: Long-term responses of atmospheric CO₂ for different weathering model variants with 4000 GtCO₂ emissions (Lenton & Britton, 2006).

Tropical regions are thought to be important for global silicate weathering rates due to the high temperatures and runoff rates (White & Blum, 1995) but climate change is expected to cause a reduce in forest cover in the tropics (IPCC, 2013). However, according to other studies based on multiple climate scenarios the risk that tropical forests are being replaced will be moderate to low (Gumpenberger et al., 2010). With the degradation of tropical forests an important factor promoting silicate weathering might disappear. Reduction of tropical forests would reduce evapotranspiration and thus runoff (IPCC, 2013). Since reduced runoff will lead to a slowdown in silicate weathering rates (Braun et al., 2005), degradation of tropical forests might lead to lower silicate weathering rates. Climate change increases the risk that the Amazon forest is being replaced by seasonal forest or savannah in the future (Malhi et al., 2009). Since Amazon forests have deeper roots than savannah and deeper roots generally result in higher silicate weathering than shallower roots (Moulton et al., 2000), the transformation to savannah might decrease silicate weathering rates. However, tropical forests might provide more shaded area to the soil. This might lower soil temperature and thus diminish silicate weathering rates. Concluding, the

possible reduction in tropical forest might affect silicate weathering rates, although it seems unclear whether this change will be positive or either negative. In contrast with the possible reduction of tropical forests, forest cover might potentially increase in the high latitude regions (IPCC, 2013).

Climate change might also account for longer dry seasons, and if the dry season becomes too long there is a larger chance that wildfires will occur and this might change the ecosystem abruptly (Malhi et al., 2009). Such abrupt ecosystem disturbances are expected to have a net positive influence on silicate weathering rates (M. A. Knoll & James, 1987). During the reestablishment of the ecosystem, the amounts of ions lost from the plant/soil system increase and this amplifies weathering rates. This is partly due to the lack of diversity in nutrient cycling and storage strategies of successional plants, which are generally annuals or short-lived perennials (Day & Monk, 1977).

Land use decisions might also play a role in silicate weathering rates in the future (Lenton & Britton, 2006). The influence of land use change on silicate weathering rates is not the same for every environment. Land use change has a negligible influence at high latitudes, but in the tropical area land use change has a large influence on runoff and thus on silicate weathering rates (Beaulieu, Godd ris, Donnadi u, Labat, & Roelandt, 2012). It is argued that over the past century land use change accounted for 50% of the global runoff increase (Piao et al., 2007) and deforestation of the Orinoco River increases CO₂ consumption by weathering over the watershed with 80% (Roelandt, Godd ris, Bonnet, & Sondag, 2010). In the mid-latitude environments land use changes are also expected to be a critical factor in silicate weathering (Beaulieu et al., 2012).

A factor that is expected to have a relatively short term influence on CaCO₃ burial in ocean sediments is ocean acidification. The largest part of fossil fuel CO₂ (70-80%) will be dissolved into ocean waters (Archer, Kheshgi, & Maier-Reimer, 1997), causing ocean acidification. Due to this ocean acidification marine CaCO₃ sediments will begin to dissolve in the coming centuries, causing the CCD to shoal. Dissolution of CaCO₃ from marine sediments adds alkalinity to the ocean. Due to this increased alkalinity, the oceans capacity to store CO₂ increases over timescales of ~5000-6000 years (Lenton & Britton, 2006). Carbonate weathering on land will also counteract ocean acidification by adding alkalinity, allowing CaCO₃ sediments to be redeposited on a timescale of ~8000 years (Archer et al., 1998). Therefore, ocean acidification only tends to have an influence on CaCO₃ burial over timescales of several thousands of years, but not on the timescales the effects of silicate weathering will play a crucial role in carbon sequestration. Eventually, in timescales of hundreds of thousands of years, ~10% of fossil fuel CO₂ is expected to be removed by silicate weathering and subsequent deposition of carbonates in the ocean (Lenton & Britton, 2006).

According to Bakker et al. (2016), the AMOC will be weakened with 18% by the year 2100 under an intermediate greenhouse-gas mitigation scenario and with 38% under continued high emissions. By the year 2300, there will be 44% likelihood of an AMOC collapse under the continued high emissions. In a modelling study over the period from the year 1800 until 2300, it

is concluded that slowdown of the AMOC is one of the dominant mechanisms in the reduction of natural carbon uptake (Matsumoto, Tokos, Chikamoto, & Ridgwell, 2010). After 10,000 years, depletion of the AMOC increases atmospheric CO₂ by 11 ppm (Chikamoto et al., 2008). On these timescales the lowered CaCO₃ production in the first 1000 years is crucial. However, over a >100,000 years' timescale, slowdown of the AMOC is expected to have negligible effect (Goodwin & Ridgwell, 2010).

Whether an area is kinetically or supply limited varies in different climatic regimes and depends on the available rock types and likely other unknown factors. Therefore, a changing climate might cause a shift in the relative dependence of silicate weathering on supply or kinetics (West et al., 2005). In many modern settings silicate weathering is supply limited, and thus there must be sufficient tectonic activity to induce enhanced silicate weathering (Foster et al., 2017). However, if tectonic activity is indeed climate dependent (Bercovici & Ricard, 2014; Foley et al., 2012) and decreases with higher surface temperatures, this will diminish the CO₂ buffering capacity of silicate weathering.

A large difference between atmospheric CO₂ level rises in the past and the anthropogenic induced rise nowadays is the timescale. For instance during the PETM the CO₂ rise occurred during 10³-10⁴ years (Penman, 2016), while nowadays it takes hundreds of years. According to a research on silicate weathering rates in the Nile Basin time lags are negligible (Bastian, Revel, Bayon, Dufour, & Vigier, 2017). In the Nile Basin during the last 32,000 years, silicate weathering rates responded abruptly to past climate changes. Studies on the Mackenzie watersheds in the arctic region and on Icelandic rivers have produced results confirming this conclusion (Beaulieu et al., 2012; Gislason et al., 2009). However, it is unknown how the extremely rapid global warming nowadays will affect calcifying organisms. According to Knoll et al. (2007) not the magnitude of the CO₂ increase is crucial for marine organisms, but the rate of the change. If CO₂ levels increase gradually over millions of years, marine organisms can adapt their physiologies. In a change over a few generations, the only possibilities for marine organisms are tolerance, migration, or death. Therefore, the overall calcite production rates in a future climate might largely depend on the adaptive response of calcifying marine organisms (O'Dea et al., 2014).

Conclusion

Climate related factors are expected to enhance silicate weathering rates in the earth's future climate. Enhanced silicate weathering might reduce atmospheric CO₂ levels to nearly pre-industrial over hundreds and thousands of years (Archer, 2005; Lenton & Britton, 2006). However, many factors that might play a crucial role in the development of the silicate weathering process are unpredictable or are not yet understood properly. For instance the influence of tectonic activity relative to climate dependent factors is still under debate. If tectonic activity turns out to have the largest impact on silicate weathering rates and thus silicate weathering turns out to be generally supply limited, climate related factors might have a minor effect on silicate weathering rates. In that situation, climate shifts will not be substantially neutralized by the effects of enhanced silicate weathering (Riebe et al., 2001). Additionally, if tectonic activity turns out to be climate related, physical erosion might be diminished in the future climate due to higher temperatures. In combination with supply limited silicate weathering, this might have a negative effect on silicate weathering rates.

Another uncertain factor that might have a large influence on silicate weathering rates is vegetation. In the tropic regions changes in vegetation might occur, whereas these areas are thought to be important for global silicate weathering rates (White & Blum, 1995). The influence of different plant species on silicate weathering rates seems to be largely unknown, and therefore the effect of vegetation changes in the tropic regions remains unknown as well. In a past climate change event the indirect effects of vegetation on silicate weathering are thought to have had a significant influence, and therefore these effects should be incorporated in research on enhanced silicate weathering as well. Thereby, in research on silicate weathering rates usually averages of large areas are used for temperature and precipitation. This method is not representative for the calculation of global silicate weathering rates (White & Blum, 1995). Additionally, land use changes including deforestation are thought to have a large impact on runoff rates and thus on silicate weathering rates, while land use changes are usually not incorporated in research on silicate weathering.

Ocean acidification and reduction of the AMOC are expected to have an influence on CaCO₃ burial in the coming thousands or ten thousands of years, but not on timescales longer than 100,000 years. However, future CaCO₃ burial might depend largely on the adaptive response of calcifying marine organisms and how this response will develop seems difficult to predict.

To determine the development of silicate weathering in our future climate, more research on several factors that might have an influence on silicate weathering rates and CaCO₃ burial is needed. Especially the influences of vegetation, tectonic activity, land use changes and the response of calcifying organisms should be understood thoroughly.

Bibliography

- Amiotte Suchet, P., Probst, J.-L., & 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 Biogeochemical Cycles*, 17(2). <https://doi.org/10.1029/2002GB001891>
- April, R., & Keller, D. (1990). Mineralogy of the rhizosphere in forest soils of the eastern United States - Mineralogic studies of the rhizosphere. *Biogeochemistry*, 9(1), 1–18. <https://doi.org/10.1007/BF00002714>
- Archer, D. (2005). Fate of fossil fuel CO₂ in geologic time. *Journal of Geophysical Research C: Oceans*. <https://doi.org/10.1029/2004JC002625>
- Archer, D. (2010). *The Global Carbon Cycle*. Oxford: Princeton University Press.
- Archer, D., Kheshgi, H., & Maier-Reimer, E. (1997). Multiple timescales for neutralization of fossil fuel CO₂. *Geophysical Research Letters*, 24(4), 405–408. <https://doi.org/10.1029/97GL00168>
- Archer, D., Kheshgi, H., & Maier-Reimer, E. (1998). Dynamics of fossil fuel CO₂ neutralization by marine CaCO₃. *Global Biogeochemical Cycles*, 12(2), 259–276. <https://doi.org/10.1029/98GB00744>
- Bakker, P., Schmittner, A., Lenaerts, J. T. M., Abe-Ouchi, A., Bi, D., van den Broeke, M. R., ... Yin, J. (2016). Fate of the Atlantic Meridional Overturning Circulation: Strong decline under continued warming and Greenland melting. *Geophysical Research Letters*, 43(23), 12,252–12,260. <https://doi.org/10.1002/2016GL070457>
- Banwart, S. A., Berg, A., & Beerling, D. J. (2009). Process-based modeling of silicate mineral weathering responses to increasing atmospheric CO₂ and climate change. *Global Biogeochemical Cycles*, 23(4). <https://doi.org/10.1029/2008GB003243>
- Bastian, L., Revel, M., Bayon, G., Dufour, A., & Vigier, N. (2017). Abrupt response of chemical weathering to Late Quaternary hydroclimate changes in northeast Africa. *Scientific Reports*, 7. <https://doi.org/10.1038/srep44231>
- Beaulieu, E., Godd ris, Y., Donnadi u, Y., Labat, D., & Roelandt, C. (2012). High sensitivity of the continental-weathering carbon dioxide sink to future climate change. *Nature Climate Change*, 2(5), 346–349. <https://doi.org/10.1038/nclimate1419>
- Bercovici, D., & Ricard, Y. (2014). Plate tectonics, damage and inheritance. *Nature*, 508(7497), 513–516. <https://doi.org/10.1038/nature13072>
- Berner, R. A. (1995). Chemical weathering and its effect on atmospheric CO₂ and climate. In S. L. Brantley & A. F. White (Eds.), *Chemical Weathering Rates of Silicate Minerals* (pp. 565–583). Washington, D.C.: Mineralogical Society of America.
- Berner, R. A., & Berner, E. K. (1997). Silicate Weathering and Climate. In W. F. Ruddiman (Ed.), *Tectonic Uplift and Climate Change* (pp. 353–365). New York and London: Plenum Press.

- Berner, R. A., Lasaga, A. C., & Garrels, R. M. (1983). The carbonate-silicate geochemical cycle and its effects on atmospheric carbon dioxide over the past 100 million years. *American Journal of Science*, 283, 641–683.
- Braun, J. J., Ndam Ngoupayou, J. R., Viers, J., Dupré, B., Bedimo Bedimo, J. P., Boeglin, J. L., ... Muller, J. P. (2005). Present weathering rates in a humid tropical watershed: Nsimi, South Cameroon. *Geochimica et Cosmochimica Acta*, 69(2), 357–387. <https://doi.org/10.1016/j.gca.2004.06.022>
- Broecker, W. S., & Sanyal, A. (1998). Does atmospheric CO₂ police the rate of chemical weathering? *Global Biogeochemical Cycles*, 12(3), 403–408. <https://doi.org/10.1029/98GB01927>
- Chikamoto, M. O., Matsumoto, K., & Ridgwell, A. (2008). Response of deep-sea CaCO₃ sedimentation to Atlantic meridional overturning circulation shutdown. *Journal of Geophysical Research: Biogeosciences*, 113(3). <https://doi.org/10.1029/2007JG000669>
- Day, F. P., & Monk, C. D. (1977). Seasonal Nutrient Dynamics in the Vegetation on a Southern Appalachian Watershed. *American Journal of Botany*, 64(9), 1126–1139. Retrieved from <http://www.jstor.org/stable/2442169>
- De La Rocha, C. L., & Conley, D. J. (2017). *Silica Stories*. Springer Nature. <https://doi.org/10.1007/978-3-319-54054-2>
- Donnadieu, Y., Goddérès, Y., & Bouttes, N. (2009). Exploring the climatic impact of the continental vegetation on the Mesozoic atmospheric CO₂ and climate history. *Climate Of The Past*, 5(1), 85–96. <https://doi.org/10.5194/cpd-4-1021-2008>
- Donnadieu, Y., Goddérès, Y., Pierrehumbert, R., Dromart, G., Jacob, R., & Fluteau, F. (2006). A GEOCLIM simulation of climatic and biogeochemical consequences of Pangea breakup. *Geochemistry, Geophysics, Geosystems*, 7(11). <https://doi.org/10.1029/2006GC001278>
- Drever, J. I. (1994). The effect of land plants on weathering rates of silicate minerals. *Geochimica et Cosmochimica Acta*, 58(10), 2325–2332. [https://doi.org/10.1016/0016-7037\(94\)90013-2](https://doi.org/10.1016/0016-7037(94)90013-2)
- Eiriksdottir, E. S., Gislason, S. R., & Oelkers, E. H. (2013). Does temperature or runoff control the feedback between chemical denudation and climate? Insights from NE Iceland. *Geochimica et Cosmochimica Acta*, 107, 65–81. <https://doi.org/10.1016/j.gca.2012.12.034>
- Elsworth, G., Galbraith, E., Halverson, G., & Yang, S. (2017). Enhanced weathering and CO₂ drawdown caused by latest Eocene strengthening of the Atlantic meridional overturning circulation. *Nature Geoscience*. <https://doi.org/10.1038/ngeo2888>
- Foley, B. J. (2015). THE ROLE OF PLATE TECTONIC–CLIMATE COUPLING AND EXPOSED LAND AREA IN THE DEVELOPMENT OF HABITABLE CLIMATES ON ROCKY PLANETS. *The Astrophysical Journal*, 812(1), 36. <https://doi.org/10.1088/0004-637X/812/1/36>
- Foley, B. J., Bercovici, D., & Landuyt, W. (2012). The conditions for plate tectonics on super-Earths: Inferences from convection models with damage. *Earth and Planetary Science Letters*, 331–332, 281–290. <https://doi.org/10.1016/j.epsl.2012.03.028>

- Foster, G. L., Royer, D. L., & Lunt, D. J. (2017). Future climate forcing potentially without precedent in the last 420 million years. *Nature Communications*, 8, 14845. <https://doi.org/10.1038/ncomms14845>
- Gaillardet, J., Dupré, B., Louvat, P., & Allègre, C. J. (1999). Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chemical Geology*, 159(1-4), 3–30. [https://doi.org/10.1016/S0009-2541\(99\)00031-5](https://doi.org/10.1016/S0009-2541(99)00031-5)
- Gislason, S. R., Oelkers, E. H., Eiriksdottir, E. S., Kardjilov, M. I., Gisladottir, G., Sigfusson, B., ... Oskarsson, N. (2009). Direct evidence of the feedback between climate and weathering. *Earth and Planetary Science Letters*, 277(1-2), 213–222. <https://doi.org/10.1016/j.epsl.2008.10.018>
- Goodwin, P., & Ridgwell, A. (2010). Ocean-atmosphere partitioning of anthropogenic carbon dioxide on multimillennial timescales. *Global Biogeochemical Cycles*, 24(2). <https://doi.org/10.1029/2008GB003449>
- Gumpenberger, M., Vohland, K., Heyder, U., Poulter, B., Macey, K., Rammig, A., ... Cramer, W. (2010). Predicting pan-tropical climate change induced forest stock gains and losses—implications for REDD. *Environmental Research Letters*, 5(1), 014013. <https://doi.org/10.1088/1748-9326/5/1/014013>
- Gwiazda, R. H., & Broecker, W. S. (1994). The separate and combined effects of temperature, soil pCO₂, and organic acidity on silicate weathering in the soil environment: Formulation of a model and results. *Global Biogeochemical Cycles*, 8(2), 141. <https://doi.org/10.1029/94GB00491>
- Harvey, L. D. D. (2000). *Global Warming: The Hard Science*. London and New York: Routledge.
- Holbourn, A., Kuhnt, W., Kochhann, K. G. D., Andersen, N., & Sebastian Meier, K. J. (2015). Global perturbation of the carbon cycle at the onset of the Miocene Climatic Optimum. *Geology*, 43(2), 123–126. <https://doi.org/10.1130/G36317.1>
- Iglesias-Rodriguez, M. D., Halloran, P. R., Rosalind, E. M. R., Ian, R. H., Colmenero-Hidalgo, E., Gittins, J. R., ... Boessenkool, K. P. (2008). Phytoplankton Calcification in a High-CO₂ World. *Science*, 320(5874), 336–340. Retrieved from <http://www.jstor.org/stable/20055028>
- IPCC. (2013). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, Cambridge and New York.
- IPCC. (2014). *Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Core Writing Team, R.K. Pachauri & L.A. Meyer (eds.)]. Cambridge and New York.
- Kelly, D. C., Nielsen, T. M. J., McCarren, H. K., Zachos, J. C., & Röhl, U. (2010). Spatiotemporal patterns of carbonate sedimentation in the South Atlantic: Implications for carbon cycling during the Paleocene-Eocene thermal maximum. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 293(1-2), 30–40. <https://doi.org/10.1016/j.palaeo.2010.04.027>

- Knoll, A. H., Bambach, R. K., Payne, J. L., Pruss, S., & Fischer, W. (2007). Paleophysiology and end-Permian mass extinction. *Earth and Planetary Science Letters*, 256, 295–313. <https://doi.org/10.1016/j.epsl.2007.02.018>
- Knoll, M. A., & James, W. C. (1987). Effect of the advent and diversification of vascular land plants on mineral weathering through geologic time. *Geology*, 15, 1099–1102.
- Kuhlbrodt, T., Griesel, A., Montoya, M., Levermann, A., Hofmann, M., & Rahmstorf, S. (2007). On the driving processes of the Atlantic meridional overturning circulation. *Reviews of Geophysics*. <https://doi.org/10.1029/2004RG000166>
- Kump, L. R., Bralower, T., & Ridgwell, A. (2009). Ocean Acidification in Deep Time. *Oceanography*, 22(4), 94–107. <https://doi.org/10.5670/oceanog.2009.100>
- Kump, L. R., Brantley, S. L., & Arthur, M. A. (2000). Chemical Weathering, Atmospheric CO₂, and Climate. *Annual Review of Earth and Planetary Sciences*, 28(1), 611–667. <https://doi.org/10.1146/annurev.earth.28.1.611>
- Le Hir, G., Donnadieu, Y., Godd eris, Y., Meyer-Berthaud, B., Ramstein, G., & Blakey, R. C. (2011). The climate change caused by the land plant invasion in the Devonian. *Earth and Planetary Science Letters*, 310(3-4), 203–212. <https://doi.org/10.1016/j.epsl.2011.08.042>
- Lenardic, A., Jellinek, A. M., & Moresi, L. N. (2008). A climate induced transition in the tectonic style of a terrestrial planet. *Earth and Planetary Science Letters*, 271(1-4), 34–42. <https://doi.org/10.1016/j.epsl.2008.03.031>
- Lenton, T. M., & Britton, C. (2006). Enhanced carbonate and silicate weathering accelerates recovery from fossil fuel CO₂ perturbations. *Global Biogeochemical Cycles*, 20(3). <https://doi.org/10.1029/2005GB002678>
- Malhi, Y., Aragao, L. E. O. C., Galbraith, D., Huntingford, C., Fisher, R., Zelazowski, P., ... Meir, P. (2009). Exploring the likelihood and mechanism of a climate-change-induced dieback of the Amazon rainforest. *Proceedings of the National Academy of Sciences*, 106(49), 20610–20615. <https://doi.org/10.1073/pnas.0804619106>
- Matsumoto, K., Tokos, K. S., Chikamoto, M. O., & Ridgwell, A. (2010). Characterizing post-industrial changes in the ocean carbon cycle in an Earth system model. *Tellus, Series B: Chemical and Physical Meteorology*, 62(4), 296–313. <https://doi.org/10.1111/j.1600-0889.2010.00461.x>
- Moulton, K. L. (1998). Quantification of the effect of plants on weathering: Studies in Iceland. *Geology*, 26(10), 895–898. [https://doi.org/10.1130/0091-7613\(1998\)026<0895:QOTEOP>2.3.CO;2](https://doi.org/10.1130/0091-7613(1998)026<0895:QOTEOP>2.3.CO;2)
- Moulton, K. L., West, A. J., & Berner, R. A. (2000). Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *American Journal of Science*, 300(7), 539–570. <https://doi.org/10.2475/ajs.300.7.539>
- O’Dea, S. A., Gibbs, Samantha, J., Bown, P. R., Young, Jeremy, R., Poulton, A. J., Newsam, C., & Wilson, P. A. (2014). Coccolithophore calcification response to past ocean acidification and climate change. *Nature Communications*, 5. <https://doi.org/10.1038/ncomms6363>

- Penman, D. E. (2016). Silicate weathering and North Atlantic silica burial during the Paleocene-Eocene Thermal Maximum. *Geology*, *44*(9), 731–734. <https://doi.org/10.1130/G37704.1>
- Piao, S., Friedlingstein, P., Ciais, P., de Noblet-Ducoudre, N., Labat, D., & Zaehle, S. (2007). Changes in climate and land use have a larger direct impact than rising CO₂ on global river runoff trends. *Proceedings of the National Academy of Sciences*, *104*(39), 15242–15247. <https://doi.org/10.1073/pnas.0707213104>
- Pogge von Strandmann, P. A. E., Vaks, A., Bar-Matthews, M., Ayalon, A., Jacob, E., & Henderson, G. M. (2017). Lithium isotopes in speleothems: Temperature-controlled variation in silicate weathering during glacial cycles. *Earth and Planetary Science Letters*, *469*, 64–74. <https://doi.org/10.1016/j.epsl.2017.04.014>
- Raymo, M. E., & Ruddiman, W. F. (1992). Tectonic forcing of late Cenozoic climate. *Nature*, *359*(6391), 117–122. <https://doi.org/10.1038/359117a0>
- Riebe, C. S., Kirchner, J. W., Granger, D. E., & Finkel, R. C. (2001). Strong tectonic and weak climatic control of long-term chemical weathering rates. *Geology*, *29*(6), 511–514. [https://doi.org/10.1130/0091-7613\(2001\)029<0511:STAWCC>2.0.CO](https://doi.org/10.1130/0091-7613(2001)029<0511:STAWCC>2.0.CO)
- Ries, J. B., Cohen, A. L., & McCorkle, D. C. (2009). Marine calcifiers exhibit mixed responses to CO₂-induced ocean acidification. *Geology*, *37*(12), 1131–1134. <https://doi.org/10.1130/G30210A.1>
- Roelandt, C., Godd eris, Y., Bonnet, M. P., & Sondag, F. (2010). Coupled modeling of biospheric and chemical weathering processes at the continental scale. *Global Biogeochemical Cycles*, *24*(2). <https://doi.org/10.1029/2008GB003420>
- Sarmiento, J. L., & Gruber, N. (2004). Calcium Carbonate Cycling. In *Ocean Biogeochemical Dynamics*. Princeton University Press.
- Sluijs, A., Schouten, S., Pagani, M., Woltering, M., Brinkhuis, H., Damst e, J. S. S., ... the Expedition 302 Scientists. (2006). Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum. *Nature*, *441*(7093), 610–613. <https://doi.org/10.1038/nature04668>
- Song, Z., Wang, H., Strong, P. J., Li, Z., & Jiang, P. (2012). Plant impact on the coupled terrestrial biogeochemical cycles of silicon and carbon: Implications for biogeochemical carbon sequestration. *Earth-Science Reviews*, *115*(4), 319–331. <https://doi.org/10.1016/j.earscirev.2012.09.006>
- Tyrrell, T. (2011). Anthropogenic modification of the oceans. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *369*(1938), 887–908. <https://doi.org/10.1098/rsta.2010.0334>
- Walker, J. C. G., Hays, P. B., & Kasting, J. F. (1981). A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. *Journal of Geophysical Research*, *86*(C10), 9776. <https://doi.org/10.1029/JC086iC10p09776>

- Wallmann, K. (2001). Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO₂ and climate. *Geochimica et Cosmochimica Acta*, 65(18), 3005–3025. [https://doi.org/10.1016/S0016-7037\(01\)00638-X](https://doi.org/10.1016/S0016-7037(01)00638-X)
- West, A. J., Galy, A., & Bickle, M. J. (2005). Tectonic and climatic controls on silicate weathering. *Earth and Planetary Science Letters*, 235(1-2), 211–228. <https://doi.org/10.1016/j.epsl.2005.03.020>
- White, A. F., & Blum, A. E. (1995). Effects of climate on chemical weathering in watersheds. *Geochimica et Cosmochimica Acta*, 59(9), 1729–1747. [https://doi.org/10.1016/0016-7037\(95\)00078-E](https://doi.org/10.1016/0016-7037(95)00078-E)
- White, A. F., Blum, A. E., Bullen, T. D., Vivit, D. V., Schulz, M., & Fitzpatrick, J. (1999). The effect of temperature on experimental and natural chemical weathering rates of granitoid rocks. *Geochimica et Cosmochimica Acta*, 63(19-20), 3277–3291. [https://doi.org/10.1016/S0016-7037\(99\)00250-1](https://doi.org/10.1016/S0016-7037(99)00250-1)
- 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.
- Zhang, Y. G., Pagani, M., Liu, Z., Bohaty, S. M., & DeConto, R. (2013). A 40-million-year history of atmospheric CO₂. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 371(2001), 20130096–20130096. <https://doi.org/10.1098/rsta.2013.0096>