Accepted for publication in Reviews of Geophysics. Copyright (2013) American Geophysical Union.
Further reproduction or electronic distribution is not permitted.

Enhanced Chemical Weathering as a Geoengineering Strategy to Reduce Atmospheric Carbon Dioxide, a Nutrient Source and to Mitigate Ocean Acidification

Authors: Jens Hartmann1), Josh West2), Phil Renforth3), Peter Köhler4), Christina L. De La Rocha5), Dieter A. Wolf-Gladrow4), Hans Dürr6), Jürgen Scheffran7)

Affiliations:
1) Institute for Biogeochemistry and Marine Chemistry, KlimaCampus, Universität Hamburg, geo@hattes.de
2) Department of Earth Sciences, University of Southern California, Los Angeles, USA
3) Department of Earth Sciences, South Parks Road, University of Oxford, Oxford, OX1 3AN United Kingdom
4) Alfred Wegener Institute for Polar and Marine Research (AWI), PO Box 12 01 61, D-27515 Bremerhaven, Germany
5) UMR CNRS 6539, Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale, Technôpole Brest-Iroise, Place Nicholas Copernic, 29280 Plouzané, France
6) Ecohydrology Group, Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON Canada
7) Institute of Geography, KlimaCampus, Universität Hamburg

Abstract:

Chemical weathering is an integral part of both the rock and carbon cycles and is being affected by changes in land use, particularly as a result of agricultural practices such as tilling, mineral fertilization, or liming to adjust soil pH. These human activities have already altered the chemical terrestrial cycles and land-ocean flux of major elements, although the extent remains difficult to quantify. When deployed on a grand scale, Enhanced Weathering (a form of mineral fertilization), the application of finely ground minerals over the land surface, could be used to remove CO_2 from the atmosphere. The release of cations during the dissolution of such silicate minerals would convert dissolved CO_2 to bicarbonate, increasing the alkalinity and pH of natural waters. Some products of mineral dissolution would precipitate in soils or taken up by ecosystems, but a significant portion would be transported to the coastal zone and the open ocean, where the increase in alkalinity would partially counteract "ocean acidification" associated with the current marked increase in atmospheric CO_2. Other elements released during this mineral dissolution, like Si, P or K, could stimulate biological productivity, further helping to remove CO_2 from the atmosphere. On land, the terrestrial carbon-pool would likely increase in response to Enhanced Weathering in areas where ecosystem growth rates are currently limited by one of the nutrients that would be released during mineral dissolution. In the ocean, the biological carbon pumps (which export organic matter and $CaCO_3$ to the deep ocean) may be altered by the resulting influx of nutrients and alkalinity to the ocean.

This review merges current interdisciplinary knowledge about Enhanced Weathering, the processes involved, and the applicability as well as some of the consequences and risks of applying the method.

Keywords: Enhanced Weathering, silicate, carbonate, agricultural practice, geoengineering, management of global matter cycles

1. Introduction

Global biogeochemical cycles have shaped the Earth's climate and surface environment since the earliest days of the planet. A profound case in point is the consumption of CO_2 during the chemical weathering of silicate rocks that has regulated the global carbon cycle, and in so doing Earth's climate over several eons [*Arvidson et al.*, 2006; *Berner*, 2004; *Kempe and Degens*, 1985; *Walker et al.*, 1981]. Today, when human perturbation of the global carbon cycle is putting social and economic stability at risk [*IPCC*, 2007], these weathering processes that have operated naturally over billions of years might be harnessed to mitigate this perturbation by accelerating the removal of CO_2 from the atmosphere. This idea of "Enhanced Weathering" by the application of powdered minerals to the land or ocean surface to facilitate accelerated dissolution) is one of several geoengineering methods gaining increasing attention as a means for avoiding potentially devastating environmental change associated with anthropogenic greenhouse gas (GHG) emissions . Enhanced Weathering techniques are already applied at restricted scales, well below that would be considered as “geoengineering”, through the application of minerals to adjust soil pH or nutrient supply (e.g., phosphorous, potassium or silica) in agricultural landscapes [*van Straaten*, 2002], but the potential of its wider application to avoid climate change and understanding consequences for global biogeochemical cycles and ecosystems is only beginning to be explored.

Enhanced Weathering has a number of potential advantages over other proposed geoengineering schemes as a method for avoiding or decelerating climate change, although much remains to be understood about how effectively it would work and what the consequences, risks and side effects might be. Enhanced chemical weathering would help remove CO_2 from the atmosphere by accelerating the natural geologic processes that transfer carbon and other elements from the rock and atmospheric reservoirs into the biosphere and ocean over time. As such, it would not, for example, require long-term storage of an enormous mass of CO_2 in the difficult to contain and potential hazardous form of a gas. And, as a side effect, it would ameliorate some of the effects of ocean acidification. However, it would alter biogeochemical cycling on local to global scales and the extent of this alteration and any secondary effects resulting from this alteration are not yet well constrained.

The purpose of this publication, which considers recent work on both the Enhanced Weathering of natural silicates, in which crushed rocks or minerals are applied to the land surface or to aquatic systems, and of artificially-produced minerals, is to stimulate discussion and further research on Enhanced Weathering. This paper begins by describing how Enhanced Weathering fits into the broader context of proposals for geoengineering and of stewardship of global biogeochemical cycles. It then briefly reviews the role of weathering in global biogeochemical cycles, introduces the use of Enhancing Weathering for CO_2 sequestration, discusses how these may affect biogeochemical cycles across a range of spatial scales (from the local or plot scale to the global scale), and explores the theoretical limitations of Enhanced Weathering as a carbon sequestration method. Finally, issues about managing Enhanced Weathering schemes are discussed. Through this, the paper aims to identify and summarize the key unknowns where targeted research could make the most significant contributions to improving our understanding of the potential effectiveness and risks of Enhanced Weathering.

1.1. Enhanced weathering as a geoengineering technology

The CO_2 emission scenarios investigated by the IPCC suggest an impending global warming of more than the 2 K suggested by the United Nations Framework Convention on Climate Change in Copenhagen in 2009 as a tolerable threshold [*Joshi et al*., 2011; *Rogelj et al*., 2011] . The most straightforward way to remain below this target would be to emit less CO_2. This would require emission reductions of as much as 30% to 85% if compared to current emissions by the year 2050 [*Solomon et al*., 2009], something which currently seems to be unlikely to occur. In a recent incantation of emissions scenarios [Meinshausen et al., 2011], the only scenario that falls short of a 2 K temperature increase is one that utilizes carbon dioxide removal (CDR) from the atmosphere [*Friedlingstein et al*., 2011]. Geoengineering, i.e., controlled and purposeful engineering at the scale of the Earth system, if well enough understood before it is deployed, may become necessary to hold global change within acceptable limits, which themselves need to be better understood and agreed upon.

Recent proposals for geoengineering of the Earth's climate fall into the categories of (a) methods for CDR (introduced above; including schemes that increase oceanic and terrestrial biomass, draw CO_2 directly out of the air, or enhanced weathering), and (b) solar radiation management (SRM) techniques, which attempt to alter the planetary energy balance by diminishing the planet's absorption of incoming solar radiation in order to optimize climate [Crutzen, 2006; *UK-Royal-Society*, 2009]. Generally speaking, SRM involves an artificial increase in extraterrestrial, atmospheric or surface albedo, leading to a higher reflectivity of the Earth and therefore to a loss of incoming solar radiation (ideas include space-based reflectors, cloud seeding, surface albedo manipulation by modification of either human settlements or man-grown vegetation, and the injection of aerosols into the stratosphere). While SRM might help to prevent excessive global warming, ignoring the effects of changes in precipitation, temperature, and sunlight on plants, it leaves the carbon cycle largely untouched in the first instance. CDR methods, on the other hand, would reduce atmospheric CO_2 and therefore work towards curing the root cause of the global warming problem. Additionally, some CDR methods, including Enhanced Weathering, would lessen ocean acidification, the "other CO_2 problem" [*Doney et al.*, 2009]. .

A more quantitative assessment of the potential of various geoengineering approaches was put forward by Lenton and Vaughan [2009], although they ignored Enhanced Weathering. They concluded that only "stratospheric aerosol injection, albedo enhancement of marine stratocumulus clouds or sunshades in space have the potential to cool the climate back towards its pre-industrial state," though strong mitigation together with CDR techniques may be able to reduce CO_2 down to pre-anthropogenic levels by the year 2100.

Since then, a variety of modeling studies have analyzed specific geoengineering approaches in greater detail, focusing mainly on SRM [e.g., *Ferraro et al.*, 2011; *Irvine et al.*, 2010; *Keith*, 2010; *Ricke et al.*, 2010] but sometimes also considering CDR [e.g., *Köhler et al.*, 2010; *Oschlies et al.*, 2010]. Recent research discusses not only the potential of each approach in terms of mitigating global warming, but increasingly considers both positive and negative effects, especially in the case of SRM, such as precipitation changes and impacts of SRM on crop yields [*Hegerl and Solomon*, 2009; *Pongratz et al.*, 2012; *Robock et al.*, 2009]. It also considers how geoengineering be used against global sea-level rise [*Irvine et al.*, 2011; *Moore et al.*, 2010], and how feedbacks between climate, vegetation, and surface albedo vary over different time periods and potential vegetation disturbance [e.g., *O'Halloran et al.*, 2012]. As yet, there is no synthesis that considers the potential of Enhanced Weathering, as well as what the range of side-effects might be. This is the purpose of the present review.

In addition to the growing discussion of the science of geoengineering, there is an ongoing debate on the policies and politics of geoengineering [e.g., *Blackstock and Long*, 2010; *Keith et al.*, 2010; *Robock et al.*, 2010]. The need to test the theoretical predictions of modeling studies with field experiments presents the problem that the safety and effectiveness of many geoengineering approaches can only be sufficiently tested at very large or even global scales. Understanding the ethical and regulatory context is critical for advancing research in this field, and details on the political and legal aspects specific to Enhanced Weathering are discussed in the supplement information.

1.2. Chemical weathering and Global Cycles of C & Si: The basic concepts

The basic understanding of how silicate weathering acts to draw down atmospheric CO_2 has been discussed at least since the work of Ebelmen [1845]. Several years thereafter, one of the first compilations of the geochemical composition of rocks and the fluvial chemical fluxes that result from chemical weathering was presented by Roth [*Roth*, 1878; 1879; 1893]. In general, the dissolution of silicate minerals (Fig. 1) consumes CO_2 because it releases cations such as Ca^{2+} and Mg^{2+} into solution, thereby increasing total alkalinity [*Wolf-Gladrow et al.*, 2007; for the definition of total alkalinity and its influence on the carabonate system, see section 2.1], drawing CO_2 into solution to form carbonate ions (CO_3^{2-}) and bicarbonate (HCO_3^-). At the typical pH values of rivers, around pH 7, most of the dissolved inorganic carbon, or DIC, exists as bicarbonate. The cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) released by chemical weathering are transported via rivers to the ocean. Over geological time scales, these cations either (i) lead to the precipitation of minerals, such as $CaCO_3$, which sequester carbon in mineral form, (ii) exchange with other elements in submarine basalts, (iii) are involved in chemical reactions during the diagenesis and alteration of sedimentary minerals on the seafloor, or (iv) are precipitated in form of evaporites [*Arvidson et al.*, 2006; *Edmond et al.*, 1979; *Elderfield and Schultz*, 1996; *Garrels and Mackenzie*, 1971; *Mackenzie and Garrels*, 1966; *Vondamm et al.*, 1985; *Wheat and Mottl*, 2000]. Over the shorter time scales of decades to centuries that are most relevant to the use of Enhanced Weathering for CO_2 sequestration, the released cations either remain in solution, thereby increasing the alkalinity of surface waters and sequestering carbon in aqueous form (as discussed at greater length in section 2), or are stored, at least temporarily, in terrestrial carbonate minerals, e.g., pedogenic carbonate [*Dart et al.*, 2007; *Manning*, 2008; *Ryskov et al.*, 2008] or adsorbed onto clay minerals and organic matter.

The effect of carbonate weathering on atmospheric CO_2 is slightly different than that of silicate weathering. Carbonate mineral precipitation releases some of the drawn-down CO_2 back to the atmosphere (Fig. 1). Carbonate weathering by carbonic acids (or organic acids derived from CO_2) can be a transient CO_2 sink when solutes are transported to the marine system, providing Ca^{2+} remains in solution together with bicarbonate ions, but once carbonate re-precipitates, there will be no net effect on atmospheric CO_2. When carbonate weathering is driven by strong acids such as HNO_3 or H_2SO_4, common anthropogenic "pollutants", it may not act as a sink of CO_2 at all, but in fact could act as source of CO_2 to the atmosphere (Fig. 1) [*Calmels et al.*, 2007; *Perrin et al.*, 2008; *Semhi et al.*, 2000]. In some natural environments this process can be driven by the oxidation of pyrite.

The total magnitude of natural weathering-associated carbon fluxes is small compared to other fluxes in the modern carbon cycle (Fig. 2), particularly if recent net influx of CO_2 to the ocean and biosphere (which is elevated due to the notable increase in atmospheric CO_2 concentrations over the last few decades) is taken into account [*Peters et al.*, 2012]. The net carbon flux from land to the ocean via rivers is ~0.8 Gt C a^{-1}, and 0.4 Gt C a^{-1} of this flux is in the form of dissolved inorganic carbon (DIC) [*IPCC*, 2007; *Ludwig et al.*, 1996; *Ludwig et al.*, 1998]. Reported global CO_2-consumption fluxes by chemical weathering range from 220 to 290 Mt C a^{-1} [Gaillardet et al., 1999; Hartmann et al., 2009]. This is smaller than the fluxes between other reservoirs, e.g., 10 Gt C a^{-1} are emitted to the atmosphere through anthropogenic activities (Fig. 2). Note that the emissions of CO_2 from limnic systems and the land-ocean transition zone are still poorly constrained and are not included in current Earth System models or global carbon budgets [c.f. the budget apporaches in: *Aufdenkampe et al.*, 2011; *IPCC*, 2007; *Peters et al.*, 2012]. Despite its small magnitude, the flux of DIC transported by rivers is thought to be important in the transfer of CO_2 out of the atmosphere over periods of time covering the glacial-interglacial cycles (100,000 years) or longer [*Pagani et al.*, 2009; *Zeebe and Caldeira*, 2008].

In addition to driving a direct drawdown of CO_2 and increase in alkalinity, silicate weathering releases dissolved silicon (DSi), a portion of which is eventually transferred to the ocean [*Dürr et al.*, 2011; *Laruelle et al.*, 2009; *Treguer et al.*, 1995]. Dissolved silicon is an important nutrient for diatoms, which produce a silicified cell-wall termed a frustule. Diatoms carry out a significant fraction of the net primary production taking place in the ocean [*Nelson et al.*, 1995; *Ragueneau et al.*, 2000; *Treguer et al.*, 1995] and play a key role in the export of particulate organic matter (POM) to the deep sea. Because this export removes Si from the surface ocean, DSi limits diatom production in large areas of the world ocean [*Dugdale and Wilkerson*, 1998].

This stimulation of diatom growth in turn means that the supply of DSi has an important influence on the marine "biological carbon pump" [*Ragueneau et al.*, 2000; *Ragueneau et al.*, 2006; *Sarmiento et al.*, 2007], a set of processes in which carbon is incorporated into particulate organic carbon (POC) through photosynthesis then exported from the surface ocean to the deep ocean before its oxidation back to CO_2 [*Boyd and Trull*, 2007; *Buesseler and Boyd*, 2009; *De La Rocha and Passow*, in press for 2012; *Honjo et al.*, 2008; *Turner*, 2002; *Volk and Hoffert*, 1985]. The carbon thus concentrated into the deep ocean is isolated from the atmosphere for the time it takes for the surface and deep ocean to mix (~1000 years, on average). Some of this POC may even be buried in marine sediments, where it can be sequestered for longer periods of time. This means that silicate weathering impacts the carbon cycle not only due to direct consumption and transfer of atmospheric carbon to the ocean associated with increased alkalinity (the purely chemical effects), but also potentially via silicon fertilization of the oceanic biological carbon pump [*Köhler et al.*, submited].

In addition, the dissolution of minerals associated with Enhanced Weathering would also be expected to release a range of other elements, some of which are key biological nutrients (e.g., P, Fe) and some of which are toxins at high concentrations (but sometimes nutrients at trace concentrations) (e.g., Cd). The exact suite and concentration of elements released will depend on the rocks selected for dissolution and clearly some caution must be exercised in this regard. The potential impacts of altering elemental fluxes to terrestrial and marine systems need to be carefully considered and further work on this front is needed for the full range of possible impacts (positive and negative) to be understood.

1.3. Proposals for Enhanced weathering

Enhancing rates of weathering could remove atmospheric carbon and store it for a significant time in terrestrial and oceanic systems, effectively accelerating the natural rate of transfer of carbon out of the atmosphere (cf. Figure 2). However, the slow natural rates of mineral weathering are a significant obstacle to overcome. The kinetics of silicate weathering per mass unit of chosen rocks can be increased by 1) increasing mineral surface area (e.g., by grinding), 2) changing the pH of reacting solutions, 3) increasing temperature, 4) increasing pressure, 5) choosing appropriate rocks with highly reactive minerals, 6) changing the flow regime and 7) making use of biological metabolism (e.g., certain plant species remove selectively released minerals and change thus the saturation state of aqueous solutions close to their root system). A strategy for Enhanced Weathering needs to make use of some combination of these means for accelerating weathering rates.

A range of strategies for Enhanced Weathering have been discussed, including:

- Spreading finely ground silicate powder, rich in easily released cations, over the terrestrial surface [*Schuiling and Krijgsman*, 2006; *Manning*, 2008]. This could enhance natural rates of chemical weathering because the large surface area of the powdered material would result in rapid dissolution of the mineral.
- Spreading artificial products like iron and steel slag and cement waste from industrial processes instead of natural silicate minerals [*Renforth et al*., 2009]. These materials dissolve rapidly and also have the potential to release CO_2-consuming cations. Similarly, silicate and carbonate materials could be treated (e.g., through calcification) to produce metal oxides (CaO, MgO) and/or carbonates which dissolve rapidly under ambient conditions [*Kheshgi*, 1995].

- Adding reactive minerals (e.g., olivine) to open ocean surface waters [*Köhler et al.*, submitted].
- Spreading suitable material into tidal areas of coastal zones [*Hangx and Spiers*, 2009], where wave action physically maintains fresh reactive surfaces, accelerating mineral dissolution and alkalinity production. In this case, the mechanical decomposition of the grains has not received much attention [*Hangx and Spiers*, 2009] but may be important to consider [*Schuiling and de Boer*, 2010; 2011].
- Pumping CO_2 into mafic and ultramafic rock formations to increase chemical weathering rates and the subsequent carbonation of minerals. This *in situ* approach is not discussed here but has been reviewed elsewhere [*Kelemen et al.*, 2011; *Oelkers et al.*, 2008]. Attention here focuses on the other low-energy, large-scale strategies for Enhanced Weathering.

The most suitable silicate mineral for Enhanced Weathering, given its reactivity and wide natural abundance, is forsterite (Mg-olivine, Fig. 1). It is characterized by a high abiotic dissolution rate per surface area when compared to other silicate minerals (Figure 3). Table 1 shows this clearly by comparing the amount of time a 1-mm grain needs to dissolve in aqueous solution at pH 5 [*Lasaga*, 1995]: a 1-mm grain of forsterite dissolves within 2300 years, while an equivalent grain of quartz requires 34 million years. A 1-mm grain of calcite dissolves in less than 1 year, so in this respect it would be an ideal mineral. However, carbonate (e.g., calcite) dissolution, as discussed above, does not necessarily lead to CO_2 sequestration (i.e., if driven by strong acids, or if it results in carbonate reprecipitation). Mafic and ultramafic rocks, which are abundant across the planet, contain a high proportion of olivine, as well as other minerals, such as pyroxene (enstatite and diopside in Table 1), with relatively high dissolution rates. This makes these relatively abundant rock types (Figure 4) ideal potential targets for Enhanced Weathering.

2. Theoretical Assessment of Enhanced Weathering of Olivine

Quantitative assessment of the scope for using Enhanced Weathering of olivine to remove CO_2 from the atmosphere is a complex endeavor. Among other things, the potential scope for CO_2 sequestration depends both on the effective sequestration capacity of the mineral, i.e., how much CO_2 is consumed per gram of olivine weathering, and on realistic rates of mineral dissolution. It is possible to place some theoretical constraints on these questions. These constraints are reviewed in this section, using forsterite (Mg-olivine) as a model mineral. The approach developed here could easily be applied to other natural minerals, or to artificial silicates, with broadly similar conclusions.

2.1. How much CO_2 is consumed per gram of olivine weathering?: Chemical basics of the marine carbonate system

The equations shown in Figure 1 provide a succinct summary of the overall net effect of weathering over the long periods of time, when carbonate precipitates locking carbon into a mineral form. However, these equations do not capture the complete effect over shorter timescales, in which dissolved cations from weathering contribute to the total alkalinity [TA: *Dickson*, 1981; *Wolf-Gladrow et al.*, 2007] of the oceans and not all cation charge supplied by weathering is balanced by increased oceanic HCO_3^- (as illustrated in the simplified equations in Figure 1). The following equations describe total alkalinity, or TA, and dissolved inorganic carbon, or DIC, of the oceans [*Zeebe and Wolf-Gladrow*, 2001].

$$(1)\ TA = [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + \left[H^+\right] + minor\ compounds$$

$$(2)\ DIC = [HCO_3^-] + [CO_3^{2-}] + [H_2CO_3^*]$$

The equilibrium constants

$$(3)\ \ K_H^* = \frac{[H_2CO_3^*]}{\left[pCO_2\ \right]}$$

$$(4)\ K_1^* = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]}$$

$$(5)\ K_2^* = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

$$(6)\ K_B^* = \frac{[B(OH)_4^-][H^+]}{[B(OH)_3\,]}$$

$$(7)\ K_w\ = [OH^-][H^+]$$

are functions of temperature, salinity, and pressure and thus differ between seawater and freshwater. The whole carbonate system shown above works in concert to determine the relative proportions of the different species of DIC. For present day sea surface conditions, the relative molar distribution of DIC into its three species H_2CO_3, HCO_3^- and CO_3^{2-} is about 1:90:9. Variations in these proportions can significantly alter the effect of weathering-derived alkalinity on the amount of CO_2 uptake from the atmosphere.

Let's consider this in the case of Mg-olivine, forsterite (referred to as olivine in the following). This mineral dissolves in water according to the following reaction:

$$(8)\,Mg_2\ SiO_4\ \ + 4\,CO_2 + 4\,H_2O\ \rightarrow 2\,Mg^{2+} + 4\,HCO_3^- +\ H_4\ SiO_4$$

This equation seems to indicate that 4 moles of CO_2 are sequestered during the dissolution of 1 mole of olivine, equivalent to 1.25 g CO_2 (or 0.34 g C) per g olivine (the molar weight of pure Mg-olivine is 140 g mol^{-1}). However, carbonate system chemistry makes the impact of Mg-olivine dissolution on the carbon cycle more complicated than suggested by Equation. 8, because both DIC and TA are changed, leading to a new, lower, steady state CO_2 concentration. Thus the ratio of CO_2 sequestration to olivine dissolution will vary with the initial state of the ocean water and with the amount of olivine dissolved. The value of 1.25 g of CO_2 per g of Mg-olivine represents an upper theoretical limit based on the stoichiometry of Eq. 8. Seawater, assumed to be initially in equilibrium with the atmosphere, will become undersaturated with respect to CO_2 by addition of TA from weathering and will slowly (over weeks to months) re-equilibrate by taking up atmospheric CO_2. The amount of CO_2 taken up by the ocean is a non-linear function of initial TA, pCO_2(atm), temperature and salinity [*Zeebe and Wolf-Gladrow*, 2001]. For large amounts of olivine, it is also a function of the amount of TA added. This makes the system seem to some extent complicated, although the calculation is straightforward for a given initial seawater composition and a given addition of alkalinity from weathering. Typical ratios of CO_2 consumption as a function of the amount of olivine-derived alkalinity added to the global oceans and for for different starting atmospheric pCO_2 are shown in Fig. 5. In general, for the ranges modelled here, the efficiency of carbon sequestration is significantly lower than the theoretical limit of 1.25g CO_2 per gram of Mg-olivine.

The surface ocean is supersaturated with respect to some carbonate minerals. Given this, the input of additional alkalinity from Enhanced Weathering might be expected to promote carbonate precipitation (see the right hand side of the carbonate equation in Figure 1), which would reduce or reverse the effectiveness of Enhanced Weathering since the carbonate precipitation reaction drives CO_2 release to the atmosphere. However, the abiotic rate of carbonate precipitation is limited in the surface ocean by the presence of sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) anions (Mg^{2+} cations also inhibit calcite precipitation) [*Berner*, 1975; *Morse et al.*, 1997; *Morse et al.*, 2007]. The limit to which the marine carbonate system can be modified before driving appreciable rates of carbonate precipitation is not fully understood, but is potentially large when distributed globally. Therefore, it is necessary to quantify the exact saturation limit for various local surface ocean conditions at which abiotic and biotic precipitation of carbonates would occur.

2.2. How much can olivine weathering rates be increased?: Abiotic kinetics of dissolution, and potential limits

Natural rates of mineral weathering and alkalinity production under ambient conditions are relatively slow and, as discussed in section 1, the associated CO_2 drawdown is small compared to other fluxes in the global carbon cycle. However, mineral dissolution rates can vary by several orders of magnitude, and facilitating rapid dissolution is a key to any Enhanced Weathering strategy. One of the most important factors controlling dissolution rates is the surface area available for reaction; higher surface area per unit mass means higher dissolution rates and greater alkalinity flux for a given mass of mineral. However, this is not the only important factor. The range of dissolution rates for olivine as a function of pH is shown in Figure 6a. There is clearly a strong dependence on pH; at low pH, olivine dissolution can proceed more rapid than at high pH. The scatter around this pH-trend in Figure 6a can partly be attributed to mineral composition, with the upper range of the scatter representing forsterite$_{100}$, effectively pure Mg-olivine. While pH and mineralogy are important controls on dissolution rate, there is still a substantial range of rates reported in the literature, even for individual minerals normalized to standard pH (Figure 6b). Variability may be due to a range of additional factors that influence dissolution rate, including temperature, solution composition, and potentially even the age of mineral surfaces.

The strong effects of pH and surface area on dissolution rate mean that finely ground olivine spread on soils will weather more rapidly than massive rock deposits, both because of the surface area production and the low pH of soil environments. This makes this a particularly attractive strategy for designing an Enhanced Weathering scheme. There is little direct experimental evidence for whether spreading olivine on soils would lead to enough of an increase in dissolution rate, as discussed below, but the initial indications are that this approach could work, especially if focused on humid and specifically tropical regions.

2.3. Estimating the potential gross global impacts of enhanced olivine weathering

There are a few key theoretical considerations when assessing the broad scope for enhanced mineral weathering on the land surface.

<u>Dissolution kinetics and the effect of saturation state:</u> Based on a consideration of solubility of silica, the runoff water volume and the constraints placed by potential changes in pH, Köhler et al. [2010] suggested roughly that the olivine dissolution technique in the moist tropics will not exceed 1 Gt C a^{-1}

(0.8 Pmol C a^{-1}). Over the next 50 years, this could sequester approximately 20 μatm of the projected 200 μatm rise in atmospheric CO_2 under the A2 emission scenario considering abiotic controlled dissolution. The key theoretical limit imposed is the decrease in mineral dissolution rate as solutions become progressively more concentrated. When solutions approach saturation, the kinetics of silicate mineral dissolution decrease and there are certain hints in literature that dissolution approaches zero or very low rates when a certain silica or ion concentrations/activities are reached [c.f. and references therein: *Lasaga et al.*, 1994; *Lasaga*, 1995; *Pokrovsky and Schott*, 2000; *VanCappellen and Qiu*, 1997a; b]. In fact, the specific effect of saturation state, or also the precipitation of secondary minerals, on forsterite dissolution rates (or other major silicate minerals) considering field conditions is poorly constrained. The basic data data for the parameterization of models and budget approaches for field conditions are needed to assess the full potential of Enhanced Weathering, specifically if the complex hydrological conditions in the soil system (e.g. variability of soil pore water content) are taken into account. While olivine is considered to be not stable under Earth surface conditions, the solubility of forsterite is predicted to be 45-60 mmol m^{-3} using published constants in the LLNL, Minteq, and wateq4f databases. This is considerably lower than the 2000 mmol m^{-3} limit imposed by Köhler et al. [2010]. Note, this discussion considers kinetics in absence of biotic processes and organic acids (c.f. discussion below).

Sequestering significant amounts of C through weathering in humid tropical regions would require extremely high weathering fluxes form the land surface. For example, over the catchment area of the Amazon, achieving sequestration of 1 Gt C a^{-1} would mean an area-normalized alkalinity production from weathering equivalent to 8.7 x 10^6 mol CO_2 km^{-2} a^{-1} [*Köhler et al.*, 2010]. This is slightly higher than the highest (to our knowledge) reported CO_2-flux measured in natural systems, of 6.4 x 10^6 mol CO_2 $km^{-2}a^{-1}$, associated with basalt weathering on the island of Java [*Dessert et al.*, 2003]. This suggests that the global limits inferred by Köhler et al. [2010] are reasonable constraints of the total maximum potential of this method.

Other studies [*Schuiling and Krijgsman*, 2006; *Wilson et al.*, 2011] suggest that weathering might be able to exceed the proposed limits. These saturation-based limits are estimated based on laboratory studies [c.f. methods used: *Berger et al.*, 1994; *Daval et al.*, 2011; *Lasaga et al.*, 1994; *Lasaga*, 1995; *Pokrovsky and Schott*, 2000; *VanCappellen and Qiu*, 1997a; b], and in principle there may be ways to overcome such limits in natural settings, such as through the formation of secondary phases. It remains difficult to assess these effects quantitatively since the range of biotic and abiotic controls on dissolution rate is not clearly understood in the context of Enhanced Weathering (see further discussion below, summarized in Table 2).

Nonetheless, it is clear that sustaining sufficiently high total weathering fluxes would require maintaining a sufficient minimum total mineral surface area for reaction. Given that dissolution is not instantaneous it might be necessary to provide a significantly larger amount of silicate powder than the target annual dissolution rate. This is illustrated by further considering the case proposed by Köhler et al. [*2010*]. They calculate that at least 3 Gt of olivine per year must be distributed over tropical soils annually for Enhanced Weathering to consume 1 Gt C a^{-1}.

To put this into the context at a local scale, global dissolution of 3 Gt of Mg-olivine per year would mean the distribution and dissolution of up to 300 g m^{-2} a^{-1} of olivine throughout the whole catchment area of the Amazon. This value assumes that 100% of the olivine that is distributed actually dissolves in the year it is applied, but this is not likely to be the case. Even far from saturation, dissolution rates are finite. Based on results of laboratory experiments [based on data in *Pokrovsky and Schott*, 2000], and assuming a grain size of 75 μm on average, at least 3000 g m^{-2} a^{-1} of olivine would need to be initially applied to offer sufficient surface area of reaction to provide the required fluxes associated with the 1 Gt C a^{-1} scenario proposed by Köhler et al. [*2010*]. This reflects a minimum estimate because it is based on weathering solutions remaining at pH 5, which is unlikely at the scale of the soil pore waters, given the likely percolation speeds [*Maher*, 2010]. Such large quantities may not need to be applied every year, as long as what is lost on an annual basis is replaced, but it is likely to be difficult to achieve sufficient alkalinity fluxes without a substantial initial application. This is clearly a very simplistic calculation, but it is valuable in demonstrating that there may be kinetic controls that make it difficult to achieve a theoretical limit considering annual application rates. The practicalities of these kinetic limits remain to be worked out definitively. For example, the amount of olivine that would be required would decrease for smaller grain sizes, as the reactive surface area per mass of mineral is increased (this is discussed in section 4.2 in detail). Biotic effects may also increase reaction rates in natural environments. Moreover, these estimates are based on washed olivine grains, and literature suggests that the initial dissolution should be higher associated with freshly crushed minerals, due to ultra-fine fragments produced from the grinding process [*Drever*, 1997]. In addition, the material loss due erosion by flooding or strong precipitation events needs to be considered.

<u>Effect of plants:</u> Ecosystem uptake of Si into the plant biomass as biogenic silica, BSi, [c.f. *Bartoli and Souchier*, 1978; *Bartoli*, 1983; *Conley*, 2002; *Fulweiler and Nixon*, 2005; *Meunier et al.*, 1999; *Street-Perrott and Barker*, 2008] might temporarily increase the total potential of mineral dissolution while decreasing the DSi soil solution concentration by shifting soil solutions further away from saturation. But the amount of Si that can conceivably be sequestered in terrestrial biomass is limited. Globally, the uptake of DSi by ecosystems is currently estimated at 60-200 Tmol Si a^{-1} globally [*Conley*, 2002]. This would equate to uptake of the Si released from dissolution of 8.4 to 28.1 Gt a^{-1} of forsterite. While this seems large, it must be taken into account that total land area suitable for olivine distribution is limited (see below). In addition, the uptake of DSi by terrestrial ecosystems is counterbalanced by an equivalent loss to the soil systems, unless there is progressive accumulation of BSi in the biomass reservoir. The amount of DSi that could be stored in the form of additional BSi is not known and depends largely on the plant communities where Enhanced Weathering would be implemented, and their capacity for silica accumulation.

<u>Effects of soil processes:</u> Further processes, like downward transport of dissolved elements in the soil column (besides efflux from the soil system through surface near runoff) and precipitation of silica [c.f. *Sommer et al.*, 2006] at depth in soils (i.e., below the zone where the olivine or other silicates are applied), affect the dissolution rate of applied minerals. The transport of dissolved products of applied

minerals from upper soil layers driven by the downward percolation of water through the soils would diminish the possibility of reaching saturated conditions under which mineral dissolution will no longer occur at significant rates. Moreover, depending on the soil type and conditions, clay formation may also depend on the DSi concentration, and could then affect the rate of applied mineral dissolution. Field experiments conducted in various environments and taking biological activity into consideration are needed to address such questions about this potential Si-saturation limit, and its effect on the weathering of olivine or other applied silicate minerals in soil environments. The review of Sommer et al. [*2006*] offers further detail on this topic.

Effects on pH of Natural Waters: Another potential limitation on olivine weathering as an Enhanced Weathering technique is the need to avoid changes in soil and river pH affecting ecosystems negatively. Dissolution of olivine or other cation-bearing silicates increases the pH of the surrounding fluids, and both terrestrial and aquatic (freshwater and marine) ecosystems are sensitive to pH variations [*Doney et al.*, 2009; *Driscoll et al.*, 2001; *Fabry et al.*, 2008; *Mayes et al.*, 2005; *Rost et al.*, 2008]. Avoiding extreme shifts in the pH of natural waters places limits on the amount of olivine weathering that can be proposed for a given river basin [c.f. example calculations in *Köhler et al.*, 2010].

2.4 Enhanced weathering by distribution of olivine in the open oceans

The limits imposed by needing to avoid large shifts in pH in freshwater systems might be avoided by dissolving olivine in the surface ocean [*Köhler et al.*, submitted] where the concentration of DSi is well below the saturation level and much larger volumes of water are involved. DSi concentrations of the modern oceans are on average ~5 mmol m^{-3} (5 μM) in the surface ocean [*Laruelle et al.*, 2009]. Even in the Southern Ocean, an exceptional region where surface water concentrations can be as high as 75 mmol m^{-3} (75 μM), concentrations remain well below amorphous silica saturation [*Koltermann et al.*, 2011] of roughly 1000 μM.

Direct dissolution of olivine in the open ocean might significantly increase the realistic scope of Enhanced Weathering with olivine (or other minerals). The CO_2 sequestration potential is slightly smaller if olivine is dissolved in the ocean compared to on land, but this effect is relatively small, and the benefit would be a faster rise in surface ocean pH (Fig. 7 D, E), a very much welcome outcome for counteracting ocean acidification [*Doney et al.*, 2009]. However, surface ocean pH is approximately 7.8-8.3, and dissolution would proceed at a much slower rate than in tropical soils (Fig. 6), thus requiring smaller mineral grain sizes for comparable dissolution rates relative to the application of the minerals onto soils). Moreover, potential complications such as the settling of grains into the deep ocean prior to their complete dissolution would have to be carefully assessed. All of the simple modeling scenarios presented here ignore the potential effects of Enhanced Weathering on the marine and terrestrial ecosystems, including the effects on the biological carbon pump and its capacity to draw down CO_2 through removal of organic biomass into the deep ocean. To the extent that it is currently possible, these aspects are discussed in detail in sections 4 and 5.

3. Empirical Insights into Enhanced Weathering

To date, no results from field experiments exploring the weathering of fine-grained olivine added to soils and the consumption of CO_2 associated with it have been published, and the authors are only are aware of only one study using pot-experiments (ten Berge et al., 2012). However, experimental evidence of studies focusing on different topics sheds light on the potential of olivine for Enhanced Weathering as a geoengineering technique and the possible consequences for global biogeochemical cycles.

3.1. Lessons from artificial silicates

One important line of evidence providing information relevant to understanding Enhanced Weathering comes from studies on the dissolution of anthropogenic material (including artificial silicates) and the formation of carbonate minerals within these materials in the natural environment. Silicate compounds are a product of numerous human activities, including mining (quarry fines and tailings), cement production and use (cement kiln dust, construction and demolition waste), iron and steel production (slag), and coal combustion (fuel ash and bottom ash) [*Renforth et al.*, 2011] and considerable work has been done to understand the fate and ecological impact of these byproducts on the natural system. These materials are usually associated with (or wholly consisting of) amorphous gels or glasses, and meta-stable crystalline phases (e.g., 'larnite,' Ca_2SiO_4 and 'alite,' Ca_3SiO_5). Given the complex mineralogy of the materials used in these experiments, computation of the weathering rate of artificial silicates is difficult. In addition to the work that has been done with artificial silicates, a substantial number of laboratory, field, and modeling studies have investigated the mineralogy, environmental chemistry, and/or carbonation of cement. These include studies of raw clinker calcium silicates and hydrated calcium silicate gels [*Bertron et al.*, 2005; *Chen et al.*, 2004; *Galle et al.*, 2004; *Hodgkinson and Hughes*, 1999; *Huntzinger et al.*, 2009; *Renforth and Manning*, 2011; *Shaw et al.*, 2000a; *Shaw et al.*, 2000b], slags and other silicate glasses [*Bayless and Schulz*, 2003; *Fredericci et al.*, 2000; *Gee et al.*, 1997; *Hamilton et al.*, 2001; *Harber and Forth*, 2001; *Huijgen et al.*, 2005; *Mayes et al.*, 2008; *Mayes et al.*, 2006; *Oelkers*, 2001; *Oelkers and Gislason*, 2001; *Parsons et al.*, 2001; *Rawlins et al.*, 2008; *Roadcap et al.*, 2005; *Sobanska et al.*, 2000] and ashes [*Dijkstra et al.*, 2006; *Goodarzi*, 2006; *Grisafe et al.*, 1988; *Gunning et al.*, 2010; *Koukouzas et al.*, 2006; *Lee and Spears*, 1997]. All studies suggest elevated reactivity in comparison to fully crystalline natural silicates.

While silicate glasses and gels are the largest component of some anthropogenic material streams (the total quantity of which may be 10-20 Gt yr^{-1}; Renforth et al., 2011), they are often also associated with other minerals. Free lime (CaO) and portlandite ($Ca(OH)_2$) are typical constituents of cements, slags and ashes [usually <15% w/w; *Das et al.*, 2007; *Koukouzas et al.*, 2006; *Scrivener et al.*, 2004], and readily carbonate in the presence of dissolved CO_2. Nonetheless, the majority of carbonate mineral formation in these waste materials is derived from the dissolution of the poorly crystalline silicate minerals. Waste materials such as these may be able to capture 190-332 Mt C a^{-1} [*Renforth et al.*, 2011]. This total carbon capture only mitigates a fraction of the carbon emissions produced during manufacturing.

Rapid carbonate mineral formation has been observed during field investigations of the weathering of artificial silicates [*Dietzel et al.*, 1992; *Kosednar-Legenstein et al.*, 2008; *Macleod et al.*, 1991; *Mayes et al.*, 2006; *Renforth et al.*, 2009; *Wilson et al.*, 2009] (Fig. 8). Renforth et al [2009] investigated the formation of carbonate in soils formed on demolition waste and slag. Figure 8 quite visibly shows carbonate formation at these sites, which is a product of rapid material weathering (equivalent to 2500 t C km^{-2} a^{-1}). In natural soils, such carbonate formation would take 100s to 1000s of years, but the rapid weathering rates of waste materials results into the observation that such a mass of carbonate is forming in only tens of years. Similarly, Wilson et al. [2009] report the sequestration of atmospheric CO_2 in 11 Mt of serpentine rich tailings at the Clinton Creek asbestos mine in Canada in 30 years. Wilson et al. [2010] interpret the stable carbon and oxygen isotope signatures in carbonates to suggest that it was the supply of carbonate ions (from the speciation of CO_2 dissolved into the aqueous phase) limiting mineral carbonate precipitation, rather than the supply of Mg^{2+} from the weathering of serpentine.

These laboratory and field investigations of artificial silicates suggest rapid weathering rates result at least in part in carbonate precipitation and thus carbon dioxide sequestration. The potentially high weathering rates identified for artificial silicates are more than an order of magnitude higher than the rates associated with natural silicate minerals (see Figure 3) and the associated CO_2 sequestration is similarly much higher than the largest identified CO_2-sequestration rates of around 75 tC km^{-2} a^{-1} associated with natural weathering, in Java and the Philippines [*Dessert et al.*, 2003; Schopka et al., 2011].

To some extent, the chemical weathering of artificial silicates deposited on the Earth surface can be considered as a practiced (albeit unintentional) application of Enhanced Weathering. Since the early 1800's, approximately 100 Gt of anthropogenic silicate material has been produced [*Renforth et al.*, 2011], and is either currently still in use or has been deposited on land (in landfills) or in the ocean. Optimizing the carbonation of these materials could on its own enhance the removal of CO_2 from the atmosphere, but optimization requires a better understanding of how and why carbonation rates vary among materials and environmental conditions. Fortunately, the rapid rates associated with artificial materials make this variability relatively easy to study, and lessons learned from such research (i.e., in terms of what most effectively increases mineral dissolution and subsequent carbonation) promise to have much wider applicability to Enhanced Weathering in general. This is thus an obvious priority area for further work.

3.2. Lessons from agriculture: Agricultural enhancement of weathering rates, and the role of liming

Additional information about Enhanced Weathering comes from our knowledge of weathering and CO_2 consumption associated with agriculture. There are indications that agricultural activities enhance weathering rates, even without the addition of reactive minerals as proposed in Enhanced Weathering strategies, though there are only a limited number of studies that have considered the impact of agricultural activities on weathering and major gaps in knowledge remain. The studies that have been done converge in suggesting that agricultural use of land increases weathering fluxes. Paces [1983] assessed the mass balance of solutes in two adjacent catchments in central Europe, one agricultural and one forested, and found that the Na flux from the agricultural catchment was 2.6±1.9 times higher than the flux from the forested catchment. When accounting for differences in the exposure of the Na-bearing oligoclase minerals, the dissolution rate constant in the agricultural catchment was found to be approximately 4.7 times higher than in the forested catchment. Similarly, Pierson-Wickmann et al. [2009] found that weathering rates under agricultural land in Brittany, France, were significantly elevated relative to trends for given runoff values for other catchments from a global compilation. Other evidence for the impact of agricultural activities on weathering rates can be observed in the long-term (~100 a) trend of increasing DIC concentration in the Mississippi River or from comparisons between forested and agricultural areas [*Barnes and Raymond*, 2009; *Raymond et al.*, 2008]. Besides agricultural land use and practices, urban areas add to the observed increased DIC fluxes [Barnes and Raymond, 2009; Moosdorf et al., 2011], whereas the contribution of suggested sources (enhanced weathering in urban green spaces, leaking sewer systems, contribution from artificial materials, groundwater resources for water supply, a.o.) to the global C-budget remains to be quantified.

Identifying the mechanism of agriculturally-Enhanced Weathering is not straightforward. One significant effect of agricultural activity is to increase the effective discharge from streams and rivers, through irrigation and a reduction in evapotranspiration [e.g., *Raymond et al.*, 2008]. Watershed-scale weathering fluxes are closely related to discharge, which (especially for peak discharge) is modified through irrigation and vegetation removal. Attention has also focused on agricultural acidification facilitating mineral dissolution, for example associated with the nitrification of nitrogen rich fertilizers [*Perrin et al.*, 2008; *Pierson-Wickmann et al.*, 2009; *Semhi et al.*, 2000]. In this case, Enhanced Weathering may not always lead to the sequestration of carbon, if DIC is associated with dissolution of carbonates by nitric acids (see Figure 1). There may also be significant effects on weathering rates from agricultural tillage, which exposes less weathered minerals from deeper soils and may enhance dissolution rates, but this latter effect is poorly quantified.

Together, these effects reflect incidental anthropogenic Enhanced Weathering as a side effect of agricultural land use [c.f. comments of *Mayorga*, 2008, on the alteration of DIC fluxes]. Better understanding of tillage and acidification as a result of N-fertilization and how they contribute to carbon fluxes associated with agriculture is clearly critical to accurately assessing the potential for CO_2 sequestration of adding new minerals to soils.

One other agricultural practice relevant to understanding Enhanced Weathering is agricultural liming. Agricultural lime (which is mostly carbonate minerals from crushed limestone, but sometimes also contains calcium or magnesium oxides) is often applied to buffer soil pH within a range favorable for crop growth [*Hamilton et al.*, 2007] or to counteract soil/stream-water acidification [*Hindar et al.*, 2003; *Huber et al.*, 2006; *Kreutzer*, 1995; *Rundle et al.*, 1995]. Several studies have explored the fate of agricultural lime applied to soils and tried to quantify its effect on CO_2 drawdown. Dissolution of carbonate minerals in agricultural lime is effectively a kind of Enhanced Weathering (cf. equations in Figure 1), where the net effect on CO_2 depends on whether dissolution is driven by carbonic acid, in which case dissolution sequesters CO_2 from the atmosphere, or by other acids, such as HNO_3 of H_2SO_4. Dissolution by the other acids leads to a loss of alkalinity in comparison to dissolution by carbonic acid (c.f. Fig 1), and may result in the addition of CO_2 to the atmosphere [*Hamilton et al.*, 2007; *Perrin et al.*, 2008; *Semhi et al.*, 2000]. This makes it difficult to accurately account for the net effect of liming practices, even when they can be directly attributed to measurable increases in riverine element fluxes [e.g., Ca^{2+} and bicarbonate; *Hartmann and Kempe*, 2008; *Oh and Raymond*, 2006]. A key distinction to liming (including the application of carbonate rocks) is that Enhanced Weathering would favour the use of silicate minerals, because these would not act as a direct CO_2 source even if they were dissolved by a strong acid (Fig. 1). Studying the effect of liming, demands in further to recognize the fact that lime addition changes the capacity of soils to act as a CO_2 sink by storing organic carbon in the long-term. While short-term studies provide partly contradicting results, a long-term study on the application of liming (~ 100a) provides evidence for a positive effect of soil organic carbon storage for grassland areas [*Fornara et al.*, 2011]. Despite the many unresolved uncertainties, the historical practice of liming provides an appealing analogue for studying Enhanced Weathering, and its potential effects, and it may be fruitful to compile gained data of the many studies undertaken in agricultural science with respect to identify under which conditions liming would result into a net carbon sink.

3.3 Need for specific experiments

It should be emphasized that, although field "experiments" such as agriculturally modified weathering, and the recarbonization rates of silicate materials associated with mining (as discussed in section 3.1), provide some guide, it remains difficult to make reliable quantitative estimates of dissolution rates associated with potential Enhanced Weathering schemes. This is because the interaction of aqueous solutions, minerals, physical soil properties, plant effects and climate variability is difficult to estimate or to model, specifically if relevant information about the physical properties of a site are weakly defined [c.f. discussion in *Godderis et al.*, 2006; *Godderis et al.*, 2009]. Such estimates will only be possible with controlled studies considering the range of processes affecting the Enhanced Weathering rate. There are several factors which complicate estimations of how quickly minerals will dissolve once applied to the land surface. In agricultural areas, the material, which has been applied directly to the soil surface, will be soon be displaced into the upper soil horizons by tilling and other agricultural practices, or be removed due to physical erosion. At the soil surface, the dissolution rate of this material will likely be controlled of the amount and chemistry of rainwater. However, mineral powder tilled below the soil surface will be additionally affected by organic acids present in soils, as well as by processes of ion exchange related to soil properties and the metabolic activity of soil organisms. In the lower horizons of the soil, CO_2 partial pressure is significantly elevated with respect to the atmosphere, due to the release of CO_2 through plant roots and to aerobic respiration that occurs within the soil and can reach temporally levels of about 50 000 ppmv, depending on land cover, soil properties, climate and season [*Flechard et al.*, 2007; *Hashimoto et al.*, 2007; *Manning and Renforth*, 2012]. Understanding the distribution of acids in the soil solution and the coincident movement of water through the soil needs some focus in future research. All of these effects will need to be carefully considered in experimental tests of Enhanced Weathering in order to derive the parameters that are needed for accurate models which predict the consequences of Enhanced Weathering applied at the large scale (Table 2).

4. Practicalities of Enhanced Weathering on Land as a climate engineering method

Few studies holistically evaluate the engineering requirements of Enhanced Weathering (including mining, crushing and milling of rocks, transportation and application), though some have begun to consider such practicalities; in particular, Hangx and Spiers [2009] investigated the potential of spreading olivine on coastal areas, and Renforth [2012] investigated the engineering requirements of deploying Enhanced Weathering at a UK national scale. Assuming optimistic weathering rates and intra-national transport distances, Renforth [2012] concluded that the energy (expressed as total thermal) requirements for Enhanced Weathering would be 2.9-91.7 GJ t^{-1} of C, and potentially cost between US$ 88-2120 t^{-1} of C. The range of the estimate is largely down to uncertainty in the grinding requirements (see below). Using these figures, a global industry that sequesters 1 Gt CO_2-C per year may have an energy demand equivalent to 0.7-19.4 % of global energy consumption. Here, the main outcomes of these studies are reviewed together with other appropriate literature, to outline the potential engineering implications of a globally operated Enhanced Weathering scheme.

4.1. Resources

Optimization of an Enhanced Weathering scheme requires identifying a highly suitable location for mineral application and connecting it to appropriate mineral resources.

Application sites: Silicate mineral dissolution rates in the environment, which are key to the feasibility of Enhanced Weathering, are known to depend on climate and mineral supply [*Dessert et al.*, 2003; *Hartmann*, 2009; *Hartmann et al.*, 2010a; *Hartmann and Moosdorf*, 2011; *West et al.*, 2005; *White and Blum*, 1995]. This means that optimal application sites would be: (i) warm and (ii) wet (such as in the humid tropics), and (iii) have a presently limited supply of readily weatherable cation-releasing minerals. Such areas with deeply weathered soils, where the upper soil is hydrologically disconnected from the weatherable rock [*Edmond et al.*, 1995; *Stallard and Edmond*, 1983; 1987; *West et al.*, 2005], are shown in Figure 9a. In addition, practicalities, including the ease of mineral application and the availability of useful infrastructure (roads, rail, inland waterways, and spreading technology for mineral addition to the land), make agricultural land (Figure 9b) most feasible for use. Thus the optimal locations for mineral application to soil are likely to be on agricultural land in the humid tropics (see Figure 9a, b).

Mineral Resources: An ideal Enhanced Weathering scheme would utilize nearby sources of rapidly dissolving silicate minerals. In general, mafic or ultramafic rocks, like peridotite, basalt, gabbro or dunite (see Figure 4) have the highest content of silicate minerals, such as olivine, that weather rapidly. Moreover, mafic and ultramafic rocks have higher cation contents than other silicate rocks, like granite or rhyolite, so called felsic rock types (Table 3), and are thus the best suited for use in Enhanced Weathering.

Mafic and ultramafic rocks are widely abundant at the Earth's surface (Figure 4), and are composed of numerous minerals. Peridotite, a rock that is effectively only composed of olivine, would be the most obvious candidate for use in Enhanced Weathering except that its distribution is relatively limited compared to other mafic rock types. Basalts, which contain mafic minerals, are primarily composed of Ca-plagioclase feldspars, pyroxene, and olivine, with minor proportions of iron (oxy)hydroxides, offer a more widely available alternative. The largest areas of basalt [Oelkers et al., 2008] are the flood basalts (e.g., Deccan Traps India, and Siberian Traps, Russia) cover several hundred thousand to a million km^2 at a depth of 1-2 km.

The distribution and abundance of ultramafic rocks are often better known on national rather than global scales. For example, Goff et al. [2000] and Krevor et al. [2009] have presented the location, within the United States, of ultramafic rocks. In the US, these rocks, which turn out to total approximately 200 km^3 of material (see Figure 4), are predominantly confined to some mountainous regions (the Appalachians in the eastern US and, in the western US, the Josephine ophiolite in Southern Oregon, Trinity ultramafic sheet and parts of the Sierra Nevada in California, and Twin Sisters dunite and Ingalls complex in Washington). To give another example on the national scale, Koukouzas et al. [2009] have estimated the carbonation potential of ultramafic rocks in the Vourinos ophiolite complex in Greece as totalling approximately 6 Gt C. Furthermore, Renforth [2012] estimates that 33 Gt of ultramafic rocks are potentially extractable in the UK, which may be able to capture approximately 7 Gt C. However, the amenity value of these formations suggests that only a fraction of this potential is exploitable.

While the quantity of material available for Enhanced Weathering may not be a limiting factor, getting it to a suitable location for weathering certainly could be. Efficient deployment of Enhanced Weathering on a global scale, requires a global and relatively high resolution compilation of geochemical rock properties that shows local and regional heterogeneities. As a starting point, global-scale assessments could be facilitated by using geochemical information from the mapping of exposed rocks (applying standardized sampling grids and interpolating between sampled sites, as has been done for Europe by the FOREGS programme [*Imrie et al*., 2008]), or by compiling regional and local geological mapping studies and assembling the geochemical properties of the rocks based on geological/lithological maps [*Hartmann et al*., 2011; *van Straaten*, 2002].

Regardless of the distribution of minerals suitable for use in Enhanced Weathering, large scale application of this geoengineering technique will require new mines; the current total global production of olivine is only ~8 Mt a^{-1} (personal communication with the Åheim mine in Norway), three orders of magnitude less than necessary for geoengineering-scale undertaking of Enhanced Weathering (see section 2). The environmental costs of such substantial additional mining, through such destructive procedures such as mountain top removal, need to be considered, as does the mobilisation of potentially hazardous metals during the dissolution of mafic and ultramafic rocks. For example, certain dunite rocks contain relatively high amounts of nickel (Ni) and and cadmium (Cd) [*Max Planck Institute for Chemistry*, 2006] and, as has been seen many times before in mine drainage, if mineral weathering releases metals at high rates, they will prove harmful to nearby ecosystems [*Alloway*, 2012]. At lower rates, however, many of the metals that would be released (e.g., Fe, Ni, Co) would serve as vital nutrients for the growth of autotrophs in terrestrial and some marine ecosystems, an effect discussed at greater length in sections 5 and 6. An overview of the significantly variable elemental composition of rocks can be found in the GEOROC-database [*Max Planck Institute for Chemistry*, 2006].

4.2. Material Processing

One of the main challenges to assessing any Enhanced Weathering strategy is determining the cost of processing the material for reaction. In particular, crushing rock ('comminution') to the particle size necessary for rapid dissolution is an energy-consuming endeavour. Some of the energy consumed in comminution is stored as potential energy of the new surface area. However, rock comminution equipment consumes substantially more energy than the theoretical free energy production of the new surface, resulting in poor efficiencies [<5%, *Fuerstenau and Abouzeid*, 2002]. Most of this energy is lost in heat, vibration and noise. Improvement of energy efficiencies in comminution would improve the feasibility and lower the cost of Enhanced Weathering.

Practical Lessons in Grinding: Rocks containing silicate minerals have long been extracted for use as aggregate that is mainly used in infrastructure development (as road base, filler in concrete, earthworks etc.). There is a lot of information available from the aggregate industry about the physical properties (particularly the particle size distribution and shape) of the material following comminution. The classic formula developed by Bond [1952], and verified by laboratory scale crushing experiments, uses particle size reduction to predict energy use in comminution:

$$W = \frac{10W_i}{\sqrt{P_{80}}} - \frac{10W_i}{\sqrt{F_{80}}} \tag{10}$$

where W_i is the material specific work index (kWh t^{-1}), P_{80} represents the particle diameter to which 80% of the product passes, F_{80} denotes the same limit in the feed. P_{80} represents a definable upper limit to the particle diameter of the resultant material. Part of this size fraction is often referred to as ‘fines’ (material that is too small for use as aggregate, usually <4 mm), which is a substantial problem in quarries. The size, and subsequent ‘quality’, of the aggregate is carefully controlled by crusher operational parameters and screens that separate out the required size fraction. Efforts are made to reduce the production of the waste fines, which are stockpiled and sometimes used in redevelopment of the site [*Woods et al.*, 2004]. Extraction and processing of metalliferous ore is not constrained in the same way, and in this case the production of fine particles (<50 μm) is desirable.

Processing rock for Enhanced Weathering would be done in several stages. First, low energy (mainly electrical ~5 kWh t^{-1}) blasting and primary crushing would be used. The majority of energy (electrical) in comminution (10-316 kWh t^{-1}; Renforth, 2012) would be used in the second step for secondary or tertiary crushing/grinding to produce the small grain sizes necessary for rapid dissolution.

Theoretical Constraints on Mechanical Grinding: Expressing energy consumption as a function of surface area is particularly useful for Enhanced Weathering, because weathering rates can also be expressed in terms of material surface area, so energy costs and weathering rates can be directly related. There have been a limited number of studies investigating surface area changes during comminution [see for example: *Axelson and Piret*, 1950; *Baláž et al.*, 2008; *Fuerstenau and Abouzeid*, 2002; *Haug et al.*, 2010; *Stamboliadis et al.*, 2009] (Figure 10). The relationship between energy consumption (y) and the resulting surface area (x) is exponential, following (Figure 10):

$$y\ \left(\frac{kWh}{t}\right) = 76.854 \pm 7.063\ e^{0.09x \pm 0.002\ \left(\frac{m^2}{g}\right)} \qquad (r^2 = 0.995) \quad (9)$$

As discussed previously (section 2), the maximum carbon capture potential of olivine is 340 kg C per tonne of mineral. If material other than pure olivine (e.g., ultramafic to mafic rocks such as dunite, which contain a small proportion of other minerals) is used, the net efficiency will decrease (~200 kg C per tonne (material) may be typical for ultrabasic rocks; Renforth, 2012; and references therein). These resources have yet to be fully quantified. Therefore, a conservative feasibility analysis of Enhanced Weathering must include the lower carbon capture potential. Furthermore, this carbon capture potential may be reduced if there is appreciable resulting carbonate precipitation in soils or the surface ocean. Fossil fuels emit approximately 0.06 to 0.27 kg C per kWh produced (0.06 kg C per kWh for road fuel, 0.11 kg C per kWh for grid electricity in the UK, ~0.27 kg C per kWh for electricity from coal combustion, see Renforth, 2012; and references therein). Therefore, the maximum energy that can be 'spent' on a material (including that which is required for extraction, processing, and transport) is between 740 and 3330 kWh per tonne of material (assuming the material can capture ~200 kg C per tonne). Exceeding this energy budget would result in material processing/transportation emissions surpassing the carbon draw-down from Enhanced Weathering. The exact energy budget for Enhanced Weathering depends on site specific information including extraction and application site infrastructure and technology, fuel mix, distance and transport mode between extraction and application site, and comminution requirements (which requires a greater understanding of weathering rates in soils). Most crushing and grinding practices use ~10^2-10^3 kWh per tonne of material (Table 4), and are generally within the range presented above.

Accounting for the energy consumed in processing is a key part of robustly determining the carbon capture efficiency of Enhanced Weathering strategies. This will need to be actively monitored since grinding efficiency may vary for different specific materials (e.g., olivine from different dunite deposits). This is important due to the trade-offs between the energy consumed in grinding, and the rate of dissolution. For example, using the energy consumption described above by Equation 9, the net CO_2 sequestration efficiency of olivine application to soils would be reduced by 5-10% because of CO_2 emissions related to the mining and grinding of olivine [*Hangx and Spiers*, 2009], assuming the use of 10 μm grain size particles. Using a 37 μm grain size would require less energy for crushing, so the loss in efficiency would only be 0.7-1.5%, but the dissolution rate of such larger sized particles is expected to be significantly slower, delaying the sequestration effect.

4.3. Transportation and infrastructure

Transportation of large quantities of milled rock requires extensive distribution networks and infrastructure [*Hangx and Spiers*, 2009]. Agricultural areas in industrialized and some emerging countries have existing supply channels and basic infrastructure that could be easily modified for use by Enhanced Weathering programs. Some areas of Africa and South East Asia, though environmentally well-suited for Enhanced Weathering, would need to build new supply channels, since there is currently little use of agricultural fertilizers and little associated infrastructure that could be co-opted for dispensing powdered minerals [*Hernandez and Torero*, 2011; *van Straaten*, 2002].

The amount of silicates that need to be transported and dissolved to implement Enhanced Weathering on a geoengineering scale is huge and may require expansion of current infrastructure even in areas where infrastructure is well developed. The olivine weathering scheme discussed here involves the production, transportation, and distribution of 3 Gt olivine per year over soils. By comparison, in 2010, a total of 8.3 Gt of goods for international trade were loaded at the world's ports (i.e., a value which does not include goods for intra-national trade [*UNCTAD*, 2011]). Thus Enhanced Weathering requires a transport industry of a scale similar to that in use for international commerce.

4.4. Application and monitoring

The application of weatherable minerals on land would preferentially be conducted using established agricultural infrastructure, including the supply chains for fertilizers. Application of ground minerals to forested regions would be a challenge since application could probably only be done from the air, at considerable expense, both financially and in terms of the carbon efficiency of CO_2 sequestration (Table 5). Application from the air would also require new infrastructure, or adaptation of existing infrastructure such as fire fighting planes, as well as a means for monitoring the amount of mineral that reaches the target soil system (a certain but unknown amount will be laterally transported by wind, and leave the optimal target area).

Indeed, independent of what minerals are used, and whether they are applied on agricultural or forested land, careful monitoring will be of paramount importance. This would have to include monitoring of:

- the chemical impact of the released solutes (including potential contaminants like heavy metals), and shifts in pH in soils and fresh water systems,
- the physical impacts of dust particles on organisms, both in aquatic systems and in the air, and
- the dissolution of the mineral powders.

Although it will not be easy to monitor of any of these aspects, tracking the dissolution of the minerals may be the hardest. It is currently difficult to make accurate predictions for how quickly the applied minerals will dissolve, much less to monitor this effect over large areas of the land surface. Any implementation of Enhanced Weathering will require the development of carefully-considered monitoring techniques for efficiency and risk assessment, as well as application strategies, which do not exist to date (c.f. supplement information).

5. Potential Feedbacks with the Terrestrial Biosphere

5.1. Plants and weathering: Beyond abiotic kinetics

In general, life across a range of scales, from microbes to forests, has been found to naturally increase rates of silicate mineral dissolution and associated drawdown of atmospheric CO_2. A key question for Enhanced Weathering is what impact biological activities would have on readily weatherable minerals applied to soils. Biological activity might increase the dissolution rate of applied minerals on the one hand, or mineral addition might reduce the biological role in weathering by altering the nutrient status of ecosystems.

Field studies have quantified to first order how the presence of plants and associated ecosystems affects mineral weathering rates. Moulton et al. [2002] compared weathering-derived element fluxes from streams draining small Icelandic catchments (basalt) that were either vegetated with birch or conifer, or covered only by lichens. They found elemental fluxes 2-5 times higher with forest vegetation compared to lichens. Bormann et al. [1998] used a mesocosm experiment at the Hubbard Brook Experimental Forest in New Hampshire, USA, where "sandboxes" with uniform granitic substrate were planted with trees or left bare. They found weathering release rates were significantly higher under the trees (18x higher for Mg and 10x for Ca). In experiments growing different plants on basaltic substrate under laboratory conditions, Hinsinger et al. [2001] found that plants enhanced the release by chemical weathering of many elements by a factor 1-5 relative to a salt solution, providing experimental evidence to support the field observations from Iceland and New Hampshire. These effects may differ depending on the tree species, for a variety of reasons such as differences in plant uptake rates of elements, soil pH and mycorrhyzal assemblages, though the relationships remain to be well understood. Some studies have hinted at higher weathering fluxes associated with angiosperms compared to gymnosperms, but this picture is not entirely conclusive [see compilation of data by *Taylor et al.*, 2009]. There is also evidence that lichens enhance weathering rates over that of bare rock, although there is a lack of well-controlled field studies to quantify this effect [c.f. *Brady et al.*, 1999; *McCarroll and Viles*, 1995].

Plants drive higher weathering rates for a number of reasons [*Manning and Renforth*, 2012]. In the process of taking up nutrient elements, they alter soil solution chemistry and change the saturation state of minerals, favouring dissolution. Through root respiration, they directly release CO_2 into soils, increasing acidity and enhancing mineral dissolution rates (see Figure 11). And, through mycorrhizal assemblages they release organic compounds that accelerate mineral dissolution [*Leake et al.*, 2008].

Some of the key mechanisms of biotic weathering enhancement involve symbiotic interactions, with plant, fungus, and bacteria communities working closely in tandem with each other. Many interactions specifically target the release of nutrient elements from minerals. In several studies, fungal hyphae have been shown to penetrate into silicate minerals to elicit the release of Ca and P from apatite [*Jongmans et al.*, 1997; *Van Breemen et al.*, 2000] which is only found in trace amounts within most rocks, but contains high concentrations of these critical nutrients. Mg and Fe are also important plant nutrients, but biological weathering of Mg- and Fe-bearing minerals (such as olivine) has not been carefully examined. The extent to which ecosystems facilitate the weathering of minerals such as olivine may depend on ecosystem nutrient status, with, for example, nutrient stress potentially driving greater biological enhancement of weathering. This should be an active area of research in terms of understanding how schemes for Enhanced Weathering will function in practice.

5.2. Release of silicon and its effects on terrestrial ecosystems

The use of silicate minerals for Enhanced Weathering will result in the production of significant quantities of dissolved silicon. This excess silicon will not be confined to soil solutions, rivers, and other aqueous systems, but will work its way into many other biogeochemical reservoirs, and may affect a range of processes in the terrestrial silica cycle (Fig. 12).

Silicon is considered to be a beneficial nutrient for plants in general, and in some cases it is essential for growth [*Epstein*, 1994; 1999; 2009]. An ample supply of usable silicon improves the water use efficiency and drought stress resilience of certain plants, increases their rate of photosynthesis under drought stress, and enhances resistance to certain diseases and infestations [*Agarie et al.*, 1992; *Chen* *et al.*, 2011; *Crusciol et al.*, 2009; *Datnoff et al.*, 1991; *Datnoff et al.*, 1992; *Datnoff et al.*, 1997; *Deren et al.*, 1994; *Gao et al.*, 2004; *Korndorfer et al.*, 1999; *Savant et al.*, 1997a; *Savant et al.*, 1997b]. This means that, in soils containing relatively low amounts of "plant-available silicon", Enhanced Weathering could improve plant health and growth. Low concentrations of plant-available silicon are found in highly weathered soils with low base cation contents, predominantly soils in regions of the humid tropics as wells as histosols with high organic matter content [*Datnoff et al.*, 1997; *Nanayakkara et al.*, 2008; *Savant et al.*, 1997a]. Many agricultural fields are also depleted in plant-available silicon because of the repeated harvesting of crops that results in the export of the silica found within plants [*Datnoff et al.*, 1997; *Nanayakkara et al.*, 2008; *Savant et al.*, 1997a]. Agricultural fields have often been fertilized with nitrate and phosphate fertilizers for years, but not with silicate, driving these fields into silicon limitation.

Silicon present in dissolved form in water is absorbed by plants as monosilicic acid, $Si(OH)_4$ [*Jones and Handreck*, 1967] where, at various deposition sites within the plants, it polymerizes into a silica gel that further condenses to form amorphous, hydrated silica solids known as phytoliths in land plants [*Yoshida et al.*, 1962]. This biogenic silica (BSi) fulfils several functions. It contributes to increases in cell wall structure, helping to defend plants against biotic stress like insect pests [*Alvarez and Datnoff*, 2001; *Deren et al.*, 1994; *Epstein*, 1999; 2009; *Ma*, 2004]. Abiotic stress reduction seems to be provided by enhancing uptake of phosphorus (in the case of rice plants), reducing toxicities associated with Mn, Fe and Al, increasing the mechanical strength of stems, improving the plant growth habit (overall shape, structure, and appearance of the plant), and reducing the shattering of grains [c.f. references in *Nanayakkara et al.*, 2008] .

Some of the observed positive effects of abundant BSi within a plant might be due to the physical properties of the phytoliths. Such silica nanoparticles possess a significant adsorption surface that could affect the wetting properties of xylem vessels (the conduit through which water is transported through vascular land plants) and thus could improve the water use efficiency of these plants [*Gao et al.*, 2006; *Gao et al.*, 2004; *Wang and Naser*, 1994; *Zwieniecki et al.*, 2001]. Increased resistance to drought has been reported for several plant species, like sorghum bicolor, maize, rye and rice, when plant available silicon has been supplied [*Chen et al.*, 2011; *Gao et al.*, 2006; *Hattori et al.*, 2005; *Hattori et al.*, 2009]. The addition of silicon to soils by enhanced chemical weathering may increase water use efficiency by as much as 35%, depending on plant species [*Gao et al.*, 2004]. This effect could mean that Enhanced Weathering, by increasing Si supply, might alter local hydrologic cycles, but this has not been carefully considered. Better understanding of this effect will be important for assessing the complete consequences of mineral application to soils.

Through the release of silicon, Enhanced Weathering could result in additional drawdown of CO_2 by stimulating plant growth in non-humid areas, because of its positive effect on the water use efficiency, and in areas where silicon is limiting to plant growth. The extent to which Enhanced Weathering could release the terrestrial biosphere from silicon limitation is not yet known, as it has only been recently recognized that land plants could be silicon limited, leaving many silicon limited regions to be identified and mapped.

It is important to recognize that most of the studies referred to in this section focused on the effect of silicon availability on agricultural ecosystems. Studies have investigated the impact of plant available silicon on the development of trees and their physiological properties for only a few species. However, recent evidence suggests that trees impact the local silica cycle differently than shrubs and grasses [c.f. the work of Cornelis: *Cornelis et al.*, 2010a; *Cornelis et al.*, 2010b; *Cornelis et al.*, 2010c; *Cornelis et al.*, 2011a; *Cornelis et al.*, 2011b], perhaps in part because BSi from forests is 10 to 15 times more soluble than BSi from grasses, owing to its greater specific surface area [*Wilding and Drees*, 1974].

5.3. Release of other nutrients and effects on ecosystem productivity

While dissolution of Mg-silicates like olivine will primarily supply Mg and Si to soils (Fig. 1), it will also release many other elements that will have effects on ecosystems. By mass, an ultramafic rock may contain up to 5% Fe, 0.06% Mn, 0.02% P, and 0.02% K [*Green*, 1964], and so weathering of 3 Gt per year of olivine could release 150 Mt Fe, and up to 1 Mt of Mn, P and K. This could spur plant growth by providing essential nutrients, thereby driving further sequestration of carbon in the terrestrial reservoir by building up standing stocks of organic carbon in biomass and soils.

The net impact of such mineral fertilization on the terrestrial carbon pool in agricultural ecosystems is already relatively well understood [e.g., *Alvarez and Datnoff*, 2001; *Ma and Takahashi*, 1990; *van Straaten*, 2002] because the optimization of crop yield and thus growth rates is a major objective in agricultural science. For example the net rice yield by application of silicon fertilizers can be increased by 10 to 50%, depending on the local conditions [c.f. in *Alvarez and Datnoff*, 2011]. The application of suitable rocks for mineral fertilization has been discussed for decades [*van Straaten*, 2002; *Walthall and Bridger*, 1943], and the large number of studies on this topic is more than can be comprehensively surveyed here.

Much less is known about the potential impact of Enhanced Weathering on the carbon content of forested regions. Tropical forested regions contain about 25% of the total terrestrial biomass [*Jobbagy and Jackson*, 2000] and account for at least 33% of the global terrestrial net primary production (NPP) [*Beer et al.*, 2010; *Grace et al.*, 1995; *Phillips et al.*, 1998]. These forests are located in the most suitable areas for carrying out Enhanced Weathering, and changes in their productivity associated with increasing nutrient supply could be significant in terms of the global carbon cycle. The main plant nutrients are N, P, and K, and a poor supply of any of these nutrients may limit productivity [*Hyvonen et al.*, 2007; *Tripler et al.*, 2006]. The mafic and ultramafic rock powders being considered for Enhanced Weathering contain minor proportions of P-rich and K-rich minerals, but little if any N, though trace metals that are present in silicate rocks are required in N-fixing enzymes [*Ragsdale*, 2009]. If tropical forest ecosystems are P- or K-limited, then the P and K supply from Enhanced Weathering should affect the carbon pool of forested ecosystems. Cleveland et al.[2011] conducted a meta-analysis for tropical forests because some studies have suggested that NPP in tropical forests is limited by P [c.f. references in *Cleveland et al.*, 2011], while others have argued that tropical forests often have a labile P pool in the surface soil sufficient to avoid P-limitation of NPP in these systems. The overall result was that the lack of spatially explicit knowledge of how tropical forest systems will react to enhanced P-availability and possibly also K-availability [*Tripler et al.*, 2006] calls for a series of large-scale nutrient manipulations experiments to clarify this issue [*Cleveland et al.*, 2011].

Based on this, we recommend that during Enhanced Weathering exercises, the effect on NPP and biomass per unit area should be monitored so that the potential surplus in C-sequestration due to biomass (and soil carbon) increase may be evaluated.

5.4. Wider consequences for agricultural systems

When minerals are spread on agricultural land during Enhanced Weathering, a significant additional benefit may be the fertilization of crops [cf. van Straaten, 2002, outlining the concept of "rocks for crops"] because silicate minerals contain most of the nutrients required by plants (with exception of N). Powdered silicate rocks have even been considered as an alternative to conventional fertilization in areas where fertilizers are not available or are too expensive for many farmers, and in organic agriculture [*Coroneos et al.*, 1995; *Leonardos et al.*, 1987; *Leonardos et al.*, 2000; *Von Fragstein et al.*, 1988; *Walthall and Bridger*, 1943]. The potential for silicates to supply K [*Manning*, 2010] is notable because this critical nutrient is rapidly depleted from agricultural soils, particularly in the tropics. Manning [2010] concludes: "the present high cost of conventional potassium fertilisers justifies further investigation of potassium silicate minerals and their host rocks (which in some cases include basic rocks, such as basalt) as alternative sources of K, especially for systems with highly weathered soils that lack a significant cation exchange capacity".

Both the time frame and exact extent of the fertilization effect of adding powdered silicate rocks to agricultural lands needs to be better assessed considering this as part of the geoengineering strategy of Enhanced Weathering. Many studies have concluded, for example, that slow dissolution and nutrient release rates from silicate minerals limit their suitability for agricultural applications [e.g., *Blum et al.*, 1989a; *Blum et al.*, 1989b; *Von Fragstein et al.*, 1988], while others have concluded that in some environments the relatively high dissolution rates of the minerals makes them suitable as long-term, slow-release fertilizers [e.g., *Leonardos et al.*, 1987; *Nkouathio et al.*, 2008]. The key lies in identifying which combinations of plants, soils, minerals, and climatic conditions result in high nutrient release rates that stimulate plant growth and crop yields. Accomplishing this is made difficult by mineral dissolution in soils being governed by a series of interactions that are difficult to simulate in laboratory experiments [*Harley and Gilkes*, 2000; *van Straaten*, 2002].What is clear is that targeted application of silicate minerals to agricultural soils may have synergistic effects on primary productivity, industrial fertilizer use, and crop yields and well-designed Enhanced Weathering schemes strategies would take advantage of this.

6. The coastal and the marine system

6.1. Total alkalinity and pH

If Enhanced Weathering is carried out on a geoengineering scale, total alkalinity (TA; see section 2, Equation 1, above) and pH in the ocean will change due to the input of the products (Mg^{2+}, Ca^{2+}, H_4SiO_4) from silicate rock weathering. The input of Mg^{2+} and Ca^{2+} leads to an immediate increase of TA (Equation 1, section 2.1). The related change of pH can be calculated under the assumption of equilibration of CO_2 partial pressures between atmosphere (a certain value given) and the ocean. The "one-time-input" weathering of 10 Pg olivine (for example pure forsterite (Mg_2SiO_4): $10*10^{15}$ g forsterite-olivine * 1/140 mol/g-forsterite * 2 mol-Magnesium/mol-forsterite), would result in an input of 1.4×10^{14} moles Mg^{2+}.

If this input were evenly distributed over the whole ocean surface (taken here as the upper 50 m of the water column), the impact on TA and pH would be relatively small ($\Delta TA = 8\ \mu mol\ kg^{-1}$, $\Delta pH = 0.001$ from an initial mean state of DIC = 2010 $\mu mol\ kg^{-1}$, TA = 2280 $\mu mol\ kg^{-1}$, T = 20°C, S = 34). However, changes in TA and pH would increase over time if the same amount of olivine was weathered every year over a longer period. If the "one-time-input" is restricted to a much smaller volume, for example just the coastal regions, the local changes in TA and pH would be much higher ($\Delta TA = 790\ \mu mol\ kg^{-1}$, $\Delta pH = 0.11$ for 1% of the upper ocean volume). The extent of the change in TA and pH in the surface ocean over time will depend in part on circulation and mixing, and thus has to be calculated using an ocean circulation model. Such detailed analysis remains to be done, so much remains to be understood about how Enhanced Weathering would influence the oceanic alkalinity system, and potentially offset the decreasing pH associated with ocean acidification [*Köhler et al.*, submitted]. Specifically, in local coastal areas affected by "acidification" due CO_2 increase in the atmosphere, the Enhanced Weathering strategy might be considered for further analysis of applicability to limit the consequences of acidification.

6.2 Alteration of the Si fluxes to the coastal zone and influence on the biological carbon pump in the oceans

In addition to changing alkalinity and pH, global scale application of Enhanced Weathering would significantly alter dissolved silicon (DSi) fluxes to the coastal zones. Silicon released by weathering on land may be transmitted, via runoff, to rivers. Some but not all of the DSi delivered to rivers is likely to be taken up as biogenic silica (BSi) produced by diatoms and marshland plants in the river, as well as in lakes, reservoirs, and estuaries [*Humborg et al.*, 1997; *Humborg et al.*, 2000; *Ittekkot et al.*, 2000]. Still, a portion of the DSi is expected to make its way into the ocean [*Laruelle et al.*, 2009], as recent retention of DSi in the land system is estimated to be only about 20% [*Beusen et al.*, 2009]. This proportion may vary locally because of varying degrees of N- and P-limitation in many large river systems draining to the coastal zone, depending in part on the industrialization-stage of the catchment and anthropogenic nutrient inputs [*Beusen et al.*, 2005; *Harrison et al.*, 2010; *Hartmann et al.*, 2010b; *Mayorga et al.*, 2010]. Moreover, while it is likely that significant amounts of BSi deposited in the flood plains of rivers is redissolved, a significant proportion might be stored in floodplain deposits, as results from the Congo river indicate [*Hughes et al.*, 2011]. However, this amount is globally uncertain and more research is needed to understand the fate of DSi during transport from its point of mobilization to the costal zones [*Hughes et al.*, 2011]. If all Si is released during the dissolution of 3 Gt of olivine in humid tropical areas (based on the scenario described in section 2), and if all of this Si reaches the coastal zone, then the annual DSi fluxes to the coastal zone in most humid tropical areas would increase by a factor of >5 over current values [c.f. *Dürr et al.*, 2011] (see Figure 13).

Several questions then arise. Will this extra DSi be entirely transmitted to and retained in nearshore sediments as BSi that has been produced by silicifying organisms (like diatoms) in the vicinity of the river plume, or will it serve as a silicon source to more distant areas of the ocean? Will this extra DSi alter marine food web structures by favoring the growth of diatoms, which, uniquely among the major marine phytoplankton, require DSi as a nutrient for growth? And, lastly, would such additional input of DSi to the ocean have any stimulating effect on the biological pumping of carbon out of the surface ocean, thereby lowering atmospheric concentrations of CO_2?

There is evidence to suggest that the enhanced delivery of DSi to the ocean by rivers would result in local, if not regional increases in the inventory of DSi in surface waters. For example, the natural DSi load in the Congo River (a flux of 3.5 x 10^{11}mol of Si per year) is enough to raise DSi concentrations along a 1000 km stretch of coastline by 5 to 10 μM [*Bernard et al.*, 2011]. In addition, the dissolution of BSi (largely produced from river-sourced DSi) from the sediments of the Congo River fan provides a diffusive supply of DSi to this area, elevating the DSi concentration of deeper waters by several μM [*Ragueneau et al.*, 2009]. Similarly, the 1.1 x 10^{12} mol per year of DSi delivered by the plume from the Amazon and Orinoco Rivers is enough to raise DSi concentrations in the Caribbean by 10 μM [*Bernard et al.*, 2011]. These are extreme cases, as the fluxes are large, but they illustrate that a doubling of the silicon flux to the ocean in specific areas could have far reaching influences of DSi concentrations in surface waters- exactly where it could be used by the obligately photosynthetic diatoms to fuel their growth.

In contrast to this, however, is the recent work of Laruelle et al [2009], who used a box model to study the impact of increasing temperatures (due to global warming) and the retention of BSi in terrestrial freshwater systems due to damming. The scenarios modeled, while focused on potential changes to the silica cycle in the near future, give some insight into the extent to which additional quantities of silicon from weathering can be transmitted from land to sea. In the model, increased temperatures, which resulted in higher weathering rates, led to consequently increased fluxes of reactive silicon towards the ocean in rivers. In the absence of increased damming, concentrations of DSi significantly increased in the coastal zone (although this may have been due not to the additional silicon per se, but to the higher dissolution rate of BSi at higher temperatures, decreasing the retention of BSi in estuaries). In the model, this additional silicon did not result in an increase in DSi concentrations in the open ocean, although, again this was due to the increase in temperature which, in the model, led to increased rates of production of BSi. When included, the projected increase in river damming diminished silicon fluxes to estuaries and the coastal zone even in the face of elevated weathering rates. It would be interesting to use such a model to explore the consequences of increasing weathering fluxes, independent of changes in temperature and subjected to various different damming scenarios, to see to what extent a sustained input of double the weathering flux of silicon could be transmitted to the coastal zone and open ocean.

It is highly probable, however, that increasing the DSi flux in rivers may shift the ecological balance in rivers, lakes, and coastal systems back towards the "natural" order that has been disrupted by damming and agricultural runoff. The 1960s through 1980s saw an explosive growth in dam building [*Rosenberg et al.*, 2000], and now about 30% of the global sediment discharge is retained behind dams rather than being transported downstream [*Vorosmarty and Sahagian*, 2000]. The trapping of amorphous (including biogenic) silica, which is easily soluble, deprives downstream areas of a significant portion of their DSi supply [*Humborg et al.*, 1997; *Humborg et al.*, 2000; *Ittekkot et al.*, 2000]. As a result, silicon fluxes to the ocean from rivers have been significantly diminished over the last century. At the same time, nitrate and phosphate fluxes to the coastal ocean have more than doubled due to runoff from agriculture [*Meybeck*, 1998]. By releasing diatoms in the coastal ocean from nitrate and/or phosphate limitation, the total amount of BSi production in coastal waters has been increased, further reducing DSi concentrations in the coastal ocean that is already being starved of silicon inputs from rivers. With lack of additional silicon input, the net result has been a shift of large freshwater systems (like the Great Lakes) and some coastal areas and seas (like the Baltic Sea and the Mississippi River plume) out of nitrogen or phosphorus limitation and into silicon limitation

[*Conley et al.*, 1993; *Nelson and Dortch*, 1996; *Turner and Rabalais*, 1994] and away from diatoms as the dominant primary producers towards groups like dinoflagellates, which are more likely to be toxic and/or prone to fall into the "harmful algal bloom" (HAB) category. It would be reasonable to expect that significant extra input of DSi to lakes, rivers, and the coastal ocean would reverse the decades-long trend away from diatoms in these areas. Whether Si release associated with Enhanced Weathering would avoid dams and reach the oceans depends on the location where minerals are applied.

If significant inputs of DSi into the coastal ocean and adjacent seas promote the growth of diatoms, will an increase in the pumping of carbon out of the surface ocean also occur? Our understanding of the myriad interacting processes and factors which control the production and destruction of rapidly sinking particles in the ocean is not yet at the point where we can make definitive predictions, especially for the coastal zone which would be the most direct recipient of the additional DSi. The answer will, both regionally and globally, depend on several things, including whether diatom growth is silicon limited (and thus stimulated by additional inputs of DSi). Also likely to play a key role is whether the extra diatom production occurs fairly continuously or in pulses (blooms) which stand a greater chance of forming and exporting large, rapidly sinking particles. And lastly, the extent to which additional dissolved silicon will result in enhanced particulate organic carbon (POC) flux out of the surface ocean will depend on whether the local food web structure favors export (e.g., in the form of appendicularian houses and salp fecal pellets) versus retention and recycling of POC in the upper water column.

There is some evidence from the open ocean that when diatoms dominate primary productivity in the ocean, they enhance the flux of POC out of the euphotic zone and into the deep ocean. This can be seen in a comparison of POC fluxes at the Hawaiian Ocean Time series (HOT) station ALOHA in the oligotrophic subtropical Pacific central gyre and at the K2 site in the northwest Pacific subarctic gyre [*Buesseler et al.*, 2007]. At the K2 site, which was dominated by diatoms, primary production was more than two times greater than at station ALOHA and a slightly greater proportion of this primary production was exported through the base of the euphotic zone (16% versus 12%). In addition, 51% of this exported POC was transferred through 500 m depth at K2 versus 20% at station ALOHA. Similarly high export efficiencies (25-40%) have been observed between 100 and 750 m depth related to a diatom bloom in the North Atlantic [*Martin et al.*, 2011]. Although differences in seasonality and food web structure between the higher and lower exporting sites may contribute to these differences in the strength and efficiency of the biological pump, at face value they suggest that diatom-dominated systems result in enhanced export of POC out of the surface ocean. Another study, based on a greater number of sites and more deeply deployed sediment traps, has noted that the silica dominated portion of the North Pacific (e.g., sites like K2) transport, on average, 214 mmol C m^{-2} y^{-1} as POC to depths of 1 km, while calcium carbonate dominated portions of the North Pacific (i.e., sites more like station ALOHA) export on average only 39 mmol C m^{-2} y^{-1}[*Honjo et al.*, 2008]. Studies incorporating plankton functional types, for what they are worth, with global circulation models suggest that diatoms are responsible for nearly the majority of POC export in the ocean [*Jin et al.*, 2006].

Although the above studies have all focused on the open ocean, diatoms are also often ecologically dominant and key contributors to particle flux in coastal zones and river plumes. It is estimated that, despite their relatively small area compared to the rest of the ocean, coastal zones comprise about 50% of both the production and sedimentary burial of BSi in the ocean [*DeMaster*, 2002; *Shipe and Brzezinski*, 2001; *Treguer and De La Rocha*, 2013 (in press)]. As continental shelves and slopes are also host to roughly 50% of the POC flux to the seabed [*Dunne et al.*, 2007], this implies a potentially strong link between diatoms and the biological carbon pump in coastal regions. That riverborne nutrients may stimulate phytoplankton growth in river plumes, not only in coastal regions adjacent to river mouths, but further at sea as well, can be seen in the elevated concentrations of BSi and significant contribution of diatoms to primary production in these plumes [e.g., *Shipe et al.*, 2006].

These studies all illustrate cases where more DSi promotes more diatom growth and greater capacity and efficiency to the export of POC to the deep sea (i.e., away from the atmosphere). In contrast, there is the entirety of the Southern Ocean which clearly demonstrates that a high availability of DSi in surface waters need not necessarily result in a high flux of POC to depth. Concentrations of DSi in Southern Ocean surface waters are remarkably high (up to 75 μM) due, in part, to the upwelling of subsurface waters with significantly high DSi concentrations. This excess of DSi, in conjunction with other environmental parameters, does result in a phytoplankton community largely dominated by diatoms. However, due to phytoplankton growth limitation by a combination of the low availability of trace metals like iron, the low availability of light related to the extremely deep surface mixed layers, the low temperatures, and the high grazing pressure relative to growth rates, overall primary production is low at 5 mol C m^{-2} y^{-1} [*Honjo et al.*, 2008] compared to the global ocean average of 12 mol C m^{-2} y^{-1}[*Field et al.*, 1998]. Roughly 11% of this net primary production in the Southern Ocean is exported to a depth of 1 km, for a flux of 69 mmol C m^{-2} y^{-1}, a value that is slightly less than half the global mean value of 120 mm C m^{-2} y^{-1} [*Honjo et al.*, 2008], but at the same time indicative of a relatively efficient biological pump.

There has also been discussion of open ocean distribution and dissolution of Si-bearing minerals as a geoengineering strategy (see section 2.4). In terms of adding DSi to the ocean, this approach would potentially overcome the bottleneck represented by river damming [*Laruelle et al.*, 2009]. Preliminary modeling results [*Köhler et al.*, submitted] with a complex ecosystem model embedded in a state-of-the-art ocean general circulation model suggest that addition and dissolution of silicate minerals in the surface ocean might change the phytoplankton species composition in the ocean towards diatoms. This study suggests that open ocean dissolution of olivine is an ocean fertilization experiment, which might also potentially have side effects typically associated with them, e.g., increase in anoxic conditions in intermediate water depths [*Lampitt et al.*, 2008].

7. Conclusions

The rapidly rising concentrations of atmospheric CO_2 are projected to significantly alter Earth's climate in a way that could be detrimental to human society and other sensitive ecosystems. At the same time, rising CO_2 is acidifying the oceans, causing harm to calcifying organisms and thereby disrupting marine food webs. Herein we have critically examined the geoengineering method of

Enhanced Weathering that has been proposed as a means of removing CO_2 from the atmosphere. We have attempted to address the practical issues and feasibility of the technique, its potential ecological impacts (positive and negative), and the infrastructure and management structures needed to both carry it out and monitor its effects.

It is worth noting that on a relatively small scale, techniques akin to Enhanced Weathering have been in use for perhaps millennia in the form of applying limestone or siliceous rock powder to condition or fertilize agricultural fields to improve productivity. These activities together with preliminary modeling and feasibility assessments suggest that Enhanced Weathering is a promising CDR (carbon dioxide removal) technique, and could be deployed as one of a portfolio of several CDR techniques to avoid or diminish impending climate change and ocean acidification.

Cation rich silicates (particularly Mg^{2+} and Ca^{2+} which are most concentrated in mafic and ultramafic rocks, with exception of carbonate rocks) are most appropriate for Enhanced Weathering. Olivine in particular represents an ideal silicate mineral. As a result of weathering, CO_2 is converted to bicarbonate and carbonate ions, which increases the alkalinity and pH of rivers and the ocean (values of which have been lowered by the increase in atmospheric CO_2). Additional solutes, like Si, P, and K, as well as a suite of trace metals, are also likely to be released, in dependence of the applied rock sources. These have the capacity to act as nutrients for plant and phytoplankton growth, potentially enhancing terrestrial and oceanic net primary productivity (including crop yields). This could further reduce the amount of CO_2 in the atmosphere by increasing terrestrial biomass (the amount of carbon held in plant tissues and soil organic matter). Likewise, the export of particulate organic carbon to the deep ocean and subsequent sedimentation could be increased if diatom growth was stimulated by the input of dissolved silicon to the coastal zone. However, our ability to predict these effects is far from definitive and impacts on marine ecosystems could be significant.

Because purposefully lowering atmospheric concentrations of CO_2 would have world-wide impacts (just as our inadvertent increasing of them does) and because the areas where Enhanced Weathering would be most successful are concentrated in the tropics, a globally relevant management plan would be essential to applying Enhanced Weathering on the scale necessary to significantly influence atmospheric CO_2 concentrations on short timescales (decades to centuries). This would entail the creation of local and regional management structures to oversee the implementation of Enhanced Weathering and to monitor its effects carefully. Significant investment in agricultural, mining, and transportation infrastructure will be required, especially in lesser developed regions, to carry out Enhanced Weathering on a large scale. Likewise, the mass of rock powder annually requiring transportation from mines and processing centers to the fields and forests of application may require a significant increase in freight capacity. As transportation is still powered by fossil fuels, substantial transportation distances (>5000 km sea freight, >200 km land freight) might reduce the effectiveness of Enhanced Weathering. The most appropriate deployment of Enhanced Weathering may use and adapt existing infrastructure from the agricultural industry.

One of the major outcomes of this review is that we do not currently know enough to be able to predict how much the fluxes of carbon and nutrients between compartments in the Earth System (soils, terrestrial biosphere, rivers, estuaries, ocean, phytoplankton, sediments) would change following geoengineering scale deployment of Enhanced Weathering. While dissolution rates of many minerals have been quantified for a wide range of environmental conditions, it is difficult to extrapolate the laboratory results to the much more complex and variable natural environment. Nonetheless, we need to improve our ability to do this, to understand the efficacy and consequences of Enhanced Weathering.

The potential negative environmental impact of Enhanced Weathering is also important to consider and investigate further (Table 6). Application of rock dust to the land surface will increase the concentration of airborne dust in the local environment. The potential risk to human and animal health may limit the appropriate application sites (away from human centres or sensitive ecosystems) or the severity of comminution. This in turn will limit the efficacy and effectiveness of Enhanced Weathering. The mobilisation of potentially toxic elements contained in some silicate rocks may detrimentally effect primary production and/or accumulate in the food chain, both of which could be harmful to human populations. Therefore an assessment of usable rocks and their locations is needed.

Studies that bridge the gap between laboratory results, local field sites and regional/global biogeochemical fluxes are strongly needed before any large scale Enhanced Weathering schemes could be undertaken (Table 7). While the consequences of not taking action against the current extremely rapid rise in CO_2 may become increasingly severe, research into Enhanced Weathering, as with any geoengineering strategy (or, more generally, any strategy to manage global biogeochemical cycles), need to be conducted in a transparent, rigorous manner, involving not just researchers, industry, and politicians, but the general public throughout the research process.

On a final note, within the next few years to decades, it may be inevitable that Enhanced Weathering is deployed, if not for its potential to sequester CO_2, then as a means of bolstering crop growth. As human population numbers continue to exponentially increase, there is increasing demand to feed more people every year. The pressure to do so may eventually result in increased application of mineral powder as fertilizer and to increase the drought tolerance and disease resistance of crops [*van Straaten*, 2002; and references provided above]. If this occurs as projected, it will significantly change the fluxes of carbon, silicon, and other biogeochemically active elements between land and ocean within the next few decades (although it would not be the first agricultural or industrial practice to do so). For this reason, it would be useful to be able to predict the ecological and biogeochemical impacts of Enhanced Weathering regardless of whether it is ever carried out for the purpose of CO_2 sequestration.

Acknowledgements:

This review was stimulated by the workshop of the Institute for Advanced Sustainability Studies on the recarbonization of the biosphere, which resulted in a publication about the recarbonization of the biosphere (Lal et al., 2012). Jens Hartmann was supported through the German Science Foundation (DFG-project HA 4472/6-1) and the Cluster of Excellence 'CliSAP' (EXC177), Universität Hamburg.

Helpful comments were provided by Mark Torres. Renforth acknowledges funding from the Oxford Martin School (University of Oxford).

References:

Agarie, S., W. Agata, F. Kubota, and P. B. Kaufman (1992), Physiological Roles of Silicon in Photosynthesis and Dry-Matter Production in Rice Plants .1. Effects of Silicon and Shading Treatments, *Jpn J Crop Sci*, *61*(2), 200-206.

Alloway, B. J. (Ed.) (2012), *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability*, 3rd ed., 697 pp., Springer,

Alvarez, J., and L. E. Datnoff (2001), The economic potential of silicon for integrated management and sustainable rice production, *Crop Prot*, *20*(1), 43-48.

Arvidson, R. S., F. T. Mackenzie, and M. Guidry (2006), MAGic: A Phanerozoic model for the geochemical cycling of major rock-forming components, *American Journal of Science*, *306*(3), 135-190.

Aufdenkampe, A. K., E. Mayorga, P. A. Raymond, J. M. Melack, S. C. Doney, S. R. Alin, R. E. Aalto, and K. Yoo (2011), Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, *Front Ecol Environ*, *9*(1), 53-60.

Axelson, J. W., and E. L. Piret (1950), Crushing of Single Particles of Crystalline Quartz - Application of Slow Compression, *Industrial & Engineering Chemistry*, *42*(4), 665-670.

Baláž, P., E. Turianicová, M. Fabián, R. A. Kleiv, J. Briancin, and A. Obut (2008), Structural changes in olivine (Mg, Fe)2SiO4 mechanically activated in high-energy mills, *International Journal of Mineral Processing*, *88*(1-2), 1-6.

Barnes, R. T., and P. A. Raymond (2009), The contribution of agricultural and urban activities to inorganic carbon fluxes within temperate watersheds, *Chemical Geology*, *266*(3-4), 318-327.

Bartholome, E., and A. S. Belward (2005), GLC2000: a new approach to global land cover mapping from Earth observation data, *International Journal of Remote Sensing*, *26*(9), 1959-1977.

Bartoli, F., and B. Souchier (1978), Cycle and Role of Biogenetic Silica in Temperate Forest Ecosystems, *Ann Sci Forest*, *35*(3), 187-202.

Bartoli, F. (1983), The Biogeochemical Cycle of Silicon in 2 Temperate Forest Ecosystems, *Ecol Bull*(35), 469-476.

Basile-Doelsch, I., J. D. Meunier, and C. Parron (2005), Another continental pool in the terrestrial silicon cycle, *Nature*, *433*(7024), 399-402.

Bayless, E. R., and M. S. Schulz (2003), Mineral precipitation and dissolution at two slag-disposal sites in northwestern Indiana, USA, *Environmental Geology*, *45*(2), 252-261.

Beer, C., et al. (2010), Terrestrial Gross Carbon Dioxide Uptake: Global Distribution and Covariation with Climate, *Science*, *329*(5993), 834-838.

Berger, G., C. Claparols, C. Guy, and V. Daux (1994), Dissolution Rate of a Basalt Glass in Silica-Rich Solutions - Implications for Long-Term Alteration, *Geochimica et Cosmochimica Acta*, *58*(22), 4875-4886.

Bernard, C. Y., H. H. Durr, C. Heinze, J. Segschneider, and E. Maier-Reimer (2011), Contribution of riverine nutrients to the silicon biogeochemistry of the global ocean - a model study, *Biogeosciences*, *8*(3), 551-564.

Berner, R. A. (1975), Role of Magnesium in Crystal-Growth of Calcite and Aragonite from Sea-Water, *Geochimica Et Cosmochimica Acta*, *39*(4), 489-&.

Berner, R. A. (2004), *The Phanerozoic Carbon Cycle: CO_2 and O_2*, Oxford University Press, Oxford, U.K.

Bertron, A., J. Duchesne, and G. Escadeillas (2005), Attack of cement pastes exposed to organic acids in manure, *Cement and Concrete Composites*, *27*(9-10), 898-909.

Beusen, A. H. W., A. L. M. Dekkers, A. F. Bouwman, W. Ludwig, and J. Harrison (2005), Estimation of global river transport of sediments and associated particulate C, N, and P, *Global Biogeochemical Cycles*, *19*(4).

Beusen, A. H. W., A. F. Bouwman, H. H. Durr, A. L. M. Dekkers, and J. Hartmann (2009), Global patterns of dissolved silica export to the coastal zone: Results from a spatially explicit global model, Global Biogeochemical Cycles, 23.

Blackstock, J. J., and J. C. S. Long (2010), The Politics of Geoengineering, Science, 327(5965), 527-527.

Blum, W. E. H., B. Herbinger, A. Mentler, F. Ottner, M. Pollack, E. Unger, and W. W. Wenzel (1989a), The use of rock powders in agri- culture. II. Efficiency of rock powders for soil amelioration, Z Pflanzenernaehr Bodenk, 152, 427-430.

Blum, W. E. H., B. Herbinger, A. Mentler, F. Ottner, M. Pollack, E. Unger, and W. W. Wenzel (1989b), The use of rock powders in agriculture. I. Chemical and mineralogical composition and suitability of rock powders for fertilization, Z Pflanzenernaehr Bodenk, 152, 421-425.

Bond, F. C. (1952), Third Theory of Comminution, Transactions of American Institute of Mining, Metallurgical, and Petroleum Engineers, 193.

Bormann, B. T., D. Wang, M. C. Snyder, F. H. Bormann, G. Benoit, and R. April (1998), Rapid, plant-induced weathering in an aggrading experimental ecosystem, Biogeochemistry, 43(2), 129-155.

Boyd, P. W., and T. W. Trull (2007), Understanding the export of biogenic particles in oceanic waters: Is there consensus?, Prog Oceanogr, 72(4), 276-312.

Brady, P. V., R. I. Dorn, A. J. Brazel, J. Clark, R. B. Moore, and T. Glidewell (1999), Direct measurement of the combined effects of lichen, rainfall, and temperature onsilicate weathering, Geochimica et Cosmochimica Acta, 63(19-20), 3293-3300.

Buesseler, K. O., et al. (2007), Revisiting carbon flux through the ocean's twilight zone, Science, 316(5824), 567-570.

Buesseler, K. O., and P. W. Boyd (2009), Shedding light on processes that control particle export and flux attenuation in the twilight zone of the open ocean, Limnol Oceanogr, 54(4), 1210-1232.

Calmels, D., J. Gaillardet, A. Brenot, and C. France-Lanord (2007), Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: Climatic perspectives, Geology, 35(11), 1003-1006.

Chapman, L. (2007), Transport and climate change: a review, J Transp Geogr, 15(5), 354-367.

Chen, J. J., J. J. Thomas, H. F. W. Taylor, and H. M. Jennings (2004), Solubility and structure of calcium silicate hydrate, Cement and Concrete Research, 34(9), 1499-1519.

Chen, W., X. Q. Yao, K. Z. Cai, and J. N. Chen (2011), Silicon Alleviates Drought Stress of Rice Plants by Improving Plant Water Status, Photosynthesis and Mineral Nutrient Absorption, Biol Trace Elem Res, 142(1), 67-76.

Cleveland, C. C., et al. (2011), Relationships among net primary productivity, nutrients and climate in tropical rain forest: a pan-tropical analysis, Ecology Letters, 14(9), 939-947.

Conley, D. J., C. L. Schelske, and E. F. Stoermer (1993), Modification of the biogeochemical cycle of silica with eutrophication, Mar Ecol-Prog Ser, 101(1-2), 179-192.

Conley, D. J. (2002), Terrestrial ecosystems and the global biogeochemical silica cycle, Global Biogeochemical Cycles, 16(4).

Cornelis, J. T., B. Delvaux, D. Cardinal, L. Andre, J. Ranger, and S. Opfergelt (2010a), Tracing mechanisms controlling the release of dissolved silicon in forest soil solutions using Si isotopes and Ge/Si ratios, Geochimica et Cosmochimica Acta, 74(14), 3913-3924.

Cornelis, J. T., B. Delvaux, and H. Titeux (2010b), Contrasting silicon uptakes by coniferous trees: a hydroponic experiment on young seedlings, Plant and Soil, 336(1-2), 99-106.

Cornelis, J. T., J. Ranger, A. Iserentant, and B. Delvaux (2010c), Tree species impact the terrestrial cycle of silicon through various uptakes, Biogeochemistry, 97(2-3), 231-245.

Cornelis, J. T., B. Delvaux, R. B. Georg, Y. Lucas, J. Ranger, and S. Opfergelt (2011a), Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: a review, Biogeosciences, 8(1), 89-112.

Cornelis, J. T., H. Titeux, J. Ranger, and B. Delvaux (2011b), Identification and distribution of the readily soluble silicon pool in a temperate forest soil below three distinct tree species, Plant and Soil, 342(1-2), 369-378.

Coroneos, C., P. Hinsinger, and R. J. Gilkes (1995), Granite powder as a source of potassium for plants: a glasshouse bioassay comparing two pasture species, Nutrient Cycling in Agroecosystems, 45(2), 143-152.

Crusciol, C. A. C., A. L. Pulz, L. B. Lemos, R. P. Soratto, and G. P. P. Lima (2009), Effects of Silicon and Drought Stress on Tuber Yield and Leaf Biochemical Characteristics in Potato, Crop Sci, 49(3), 949-954.

Crutzen, P. J. (2006), Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma?, Climatic Change, 77(3-4), 211-219.

Dart, R. C., K. M. Barovich, D. J. Chittleborough, and S. M. Hill (2007), Calcium in regolith carbonates of central and southern Australia:Its source and implications for the global carbon cycle, Palaeogeography, Palaeoclimatology, Palaeoecology, 249(3-4), 322-334.

Das, B., S. Prakash, P. S. R. Reddy, and V. N. Misra (2007), An overview of utilization of slag and sludge from steel industries, Resources, Conservation and Recycling, 50(1), 40-57.

Datnoff, L. E., R. N. Raid, G. H. Snyder, and D. B. Jones (1991), Effect of Calcium Silicate on Blast and Brown Spot Intensities and Yields of Rice, Plant Dis, 75(7), 729-732.

Datnoff, L. E., G. H. Snyder, and C. W. Deren (1992), Influence of Silicon Fertilizer Grades on Blast and Brown Spot Development and on Rice Yields, Plant Dis, 76(10), 1011-1013.

Datnoff, L. E., C. W. Deren, and G. H. Snyder (1997), Silicon fertilization for disease management of rice in Florida, Crop Prot, 16(6), 525-531.

Daval, D., et al. (2011), Influence of amorphous silica layer formation on the dissolution rate of olivine at 90 degrees C and elevated pCO_2, Chemical Geology, 284(1-2), 193-209.

De La Rocha, C. L., and U. Passow (in press for 2012), The biological pump, in The Oceans and Marine Geochemistry, edited by M. J. Mottl, Elsevier.

DeMaster, D. J. (2002), The accumulation and cycling of biogenic silica in the Southern Ocean: revisiting the marine silica budget, Deep-Sea Res Pt Ii, 49(16), 3155-3167.

Deren, C. W., L. E. Datnoff, G. H. Snyder, and F. G. Martin (1994), Silicon Concentration, Disease Response, and Yield Components of Rice Genotypes Grown on Flooded Organic Histosols, Crop Sci, 34(3), 733-737.

Dessert, C., B. Dupre, J. Gaillardet, L. M. Francois, and C. J. Allegre (2003), Basalt weathering laws and the impact of basalt weathering on the global carbon cycle, Chemical Geology, 202, 257-273.

Dickson, A. G. (1981), An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data, Deep-Sea Research, 28A(6), 609-623.

Dietzel, M., E. Usdowski, and J. Hoefs (1992), Chemical and $^{13}C/^{12}C$- and $^{18}O/^{16}O$-isotope evolution of alkaline drainage waters and the precipitation of calcite, Applied Geochemistry, 7(2), 177-184.

Dijkstra, J. J., H. A. van der Sloot, and R. N. J. Comans (2006), The leaching of major and trace elements from MSWI bottom ash as a function of pH and time, Applied Geochemistry, 21(2), 335-351.

Doney, S. C., V. J. Fabry, R. A. Feely, and J. A. Kleypas (2009), Ocean Acidification: The Other CO_2 Problem, Annu Rev Mar Sci, 1, 169-192.

Drever, J. I. (1997), The geochemistry of natural waters, 1-436 pp., Prentice-Hall, Upper Saddle River.

Driscoll, C. T., G. B. Lawrence, A. J. Bulger, T. J. Butler, C. S. Cronan, C. Eagar, K. F. Lambert, G. E. Likens, J. L. Stoddard, and K. C. Weathers (2001), Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies, Bioscience, 51(3), 180-198.

Dugdale, R. C., and F. P. Wilkerson (1998), Silicate regulation of new production in the equatorial Pacific upwelling, Nature, 391(6664), 270-273.

Dunne, J. P., J. L. Sarmiento, and A. Gnanadesikan (2007), A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor, Global Biogeochemical Cycles, 21(4).

Dürr, H. H., M. Meybeck, J. Hartmann, G. G. Laruelle, and V. Roubeix (2011), Global spatial distribution of natural riverine silica inputs to the coastal zone, Biogeosciences, 8(3), 597-620.

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

Edmond, J. M., C. Measures, R. E. Mcduff, L. H. Chan, R. Collier, B. Grant, L. I. Gordon, and J. B. Corliss (1979), Ridge Crest Hydrothermal Activity and the Balances of the Major and Minor Elements in the Ocean - Galapagos Data, Earth and Planetary Science Letters, 46(1), 1-18.

Edmond, J. M., M. R. Palmer, C. I. Measures, B. Grant, and R. F. Stallard (1995), The Fluvial Geochemistry and Denudation Rate of the Guayana Shield in Venezuela, Colombia, and Brazil, Geochimica et Cosmochimica Acta, 59(16), 3301-3325.

Elderfield, H., and A. Schultz (1996), Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean, Annu Rev Earth Pl Sc, 24, 191-224.

Epstein, E. (1994), The Anomaly of Silicon in Plant Biology, P Natl Acad Sci USA, 91(1), 11-17.

Epstein, E. (1999), Silicon, Annu Rev Plant Phys, 50, 641-664.

Epstein, E. (2009), Silicon: its manifold roles in plants, Ann Appl Biol, 155(2), 155-160.

Etheridge, D. M., L. P. Steele, R. L. Langenfelds, R. J. Francey, J. M. Barnola, and V. I. Morgan (1996), Natural and anthropogenic changes in atmospheric CO_2 over the last 1000 years from air in Antarctic ice and firn, J Geophys Res-Atmos, 101(D2), 4115-4128.

Fabry, V. J., B. A. Seibel, R. A. Feely, and J. C. Orr (2008), Impacts of ocean acidification on marine fauna and ecosystem processes, Ices J Mar Sci, 65(3), 414-432.

FAO, IIASA, ISRIC, ISSCAS, and JRC (2008), Harmonized World Soil Database (version 1.0), edited by R. FAO, Italy and IIASA, FAO, Rome, Italy and IIASA.

Ferraro, A. J., E. J. Highwood, and A. J. Charlton-Perez (2011), Stratospheric heating by potential geoengineering aerosols, Geophys Res Lett, 38.

Field, C. B., M. J. Behrenfeld, J. T. Randerson, and P. Falkowski (1998), Primary production of the biosphere: Integrating terrestrial and oceanic components, Science, 281(5374), 237-240.

Flechard, C. R., A. Neftel, M. Jocher, C. Ammann, J. Leifeld, and J. Führer (2007), Temporalchanges in soilporespace CO_2 concentration and storage under permanent grassland, Agricultural and Forest Meteorology, 142(1), 66-84.

Fornara, D. A., S. Steinbeiss, N. P. McNamara, G. Gleixner, S. Oakley, P. R. Poulton, A. J. Macdonald, and R. D. Bardgett (2011), Increases in soil organic carbon sequestration can reduce the global warming potential of long-term liming to permanent grassland, Global Change Biol, 17(5), 1925-1934.

Fredericci, C., E. D. Zanotto, and E. C. Ziemath (2000), Crystallization mechanism and properties of a blast furnace slag glass, Journal of non-crystalline solids 273, 64-75.

Friedlingstein, P., et al. (2006), Climate-carbon cycle feedback analysis: Results from the (CMIP)-M-4 model intercomparison, J Climate, 19(14), 3337-3353.

Friedlingstein, P., S. Solomon, G. K. Plattner, R. Knutti, P. Ciais, and M. R. Raupach (2011), Long-term climate implications of twenty-first century options for carbon dioxide emission mitigation, Nat Clim Change, 1(9), 457-461.

Fuerstenau, D. W., and A. Z. M. Abouzeid (2002), The energy efficiency of ball milling in comminution, International Journal of Mineral Processing, 67(1-4), 161-185.

Fulweiler, R. W., and S. W. Nixon (2005), Terrestrial vegetation and the seasonal cycle of dissolved silica in a southern New England coastal river, Biogeochemistry, 74(1), 115-130.

Gaillardet, J., B. Dupré, P. Louvat, and C. J. Allègre (1999), Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers, *Chemical Geology*, *159*(1-4), 3-30.

Galle, C., H. Peycelon, and R. Le Bescop (2004), Effect of an accelerated chemical degradation on water permeability and pore structure of cement-based materials, Adv. Cem. Res., 16(3), 105-114.

Gao, X. P., C. Q. Zou, L. J. Wang, and F. S. Zhang (2006), Silicon decreases transpiration rate and conductance from stomata of maize plants, J Plant Nutr, 29(9), 1637-1647.

Gao, Y. B., C. C. Ma, Q. F. Li, and T. R. Xin (2004), Effects of silicon application on drought resistance of cucumber plants, Soil Sci Plant Nutr, 50(5), 623-632.

Garrels, R. M., and F. T. Mackenzie (1971), The evolution of sedimentary rocks, 1-397 pp., Norton, New York.

Gee, C., M. H. Ramsey, J. Maskall, and I. Thornton (1997), Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead, Journal of Geochemical Exploration, 58(2-3), 249-257.

Godderis, Y., L. M. Francois, A. Probst, J. Schott, D. Moncoulon, D. Labat, and D. Viville (2006), Modelling weathering processes at the catchment scale: The WITCH numerical model, Geochimica et Cosmochimica Acta, 70(5), 1128-1147.

Godderis, Y., C. Roelandt, J. Schott, M. C. Pierret, and L. M. Francois (2009), Towards an Integrated Model of Weathering, Climate, and Biospheric Processes, Reviews in Mineralogy & Geochemistry, 70, 411-434.

Goff, F., G. Guthrie, B. Lipin, M. Fite, D. Counce, E. Kluk, and H. Ziock (2000), Evaluation of Ultramafic Deposits in the Eastern United States and Puerto Rico as Sources of Magnesium for Carbon Dioxide Sequestration, Rep., Los Alamos National Laboratory.

Goldich, S. S. (1938), A Study in Rock-Weathering, The Journal of Geology, 46(1), 17-58.

Golubev, S. V., and O. S. Pokrovsky (2006), Experimental study of the effect of organic ligands on diopside dissolution kinetics, Chemical Geology, 235(3-4), 377-389.

Goodarzi, F. (2006), Characteristics and composition of fly ash from Canadian coal-fired power plants, Fuel, 85(10-11), 1418-1427.

Grace, J., et al. (1995), Carbon-Dioxide Uptake by an Undisturbed Tropical Rain-Forest in Southwest Amazonia, 1992 to 1993, Science, 270(5237), 778-780.

Green, D. H. (1964), The Petrogenesis of the High-Temperature Peridotite Intrusion in the Lizard Area, Cornwall, Journal of Petrology, 5(1), 134-188.

Grisafe, D. A., E. E. Angino, and S. S. Smith (1988), Leaching characteristics of a high calcium fly ash as a function of pH: A potential source of selenium toxicity, Applied Geochemistry, 3, 601–608.

Gunning, P. J., C. D. Hills, and P. J. Carey (2010), Accelerated carbonation treatment of industrial wastes, Waste Management, 30(6), 1081-1090.

Hamilton, J. P., S. L. Brantley, C. G. Pantano, L. J. Criscenti, and J. D. Kubicki (2001), Dissolution of nepheline, jadeite and albite glasses: toward better models for aluminosilicate dissolution, Geochimica Et Cosmochimica Acta, 65(21), 3683-3702.

Hamilton, S. K., A. L. Kurzman, C. Arango, L. X. Jin, and G. P. Robertson (2007), Evidence for carbon sequestration by agricultural liming, Global Biogeochemical Cycles, 21(2), GB2021.

Hangx, S. J. T., and C. J. Spiers (2009), Coastal spreading of olivine to control atmospheric CO(2) concentrations: A critical analysis of viability, Int J Greenh Gas Con, 3(6), 757-767.

Harber, A. J., and R. A. Forth (2001), The contamination of former iron and steel works sites, Environmental Geology, 40(3), 324-330.

Harley, A. D., and R. J. Gilkes (2000), Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview, Nutrient Cycling in Agroecosystems, 56(1), 11-36.

Harrison, J. A., A. F. Bouwman, E. Mayorga, and S. Seitzinger (2010), Magnitudes and sources of dissolved inorganic phosphorus inputs to surface fresh waters and the coastal zone: A new global model, Global Biogeochemical Cycles, 24.

Hartmann, J., and S. Kempe (2008), What is the maximum potential for CO$_2$ sequestration by "stimulated" weathering on the global scale?, Naturwissenschaften, DOI: 10.1007/s00114-008-0434-4.

Hartmann, J. (2009), Bicarbonate-fluxes and CO2-consumption by chemical weathering on the Japanese Archipelago - Application of a multi-lithological model framework, Chemical Geology, 265(3-4), 237-271.

Hartmann, J., N. Jansen, H. H. Dürr, S. Kempe, and P. Köhler (2009), Global CO$_2$-consumption by chemical weathering: What is the contribution of highly active weathering regions?, Global and Planetary Change, 69(4), 185-194.Hartmann, J., N. Jansen, H. H. Dürr, A. Harashima, K. Okubo, and S. Kempe (2010a), Predicting riverine dissolved silica fluxes to coastal zones from a hyperactive region and analysis of their first-order controls, International Journal of Earth Sciences, 99(1), 207-230.

Hartmann, J., J. K. Levy, and S. Kempe (2010b), Increasing dissolved silica trends in the Rhine River: an effect of recovery from high P loads?, Limnology, doi: 10.1007/s10201-010-0322-4, 1-11.

Hartmann, J., H. H. Dürr, N. Moosdorf, S. Kempe, and M. Meybeck (2011), The geochemical composition of the terrestrial surface (without soils) and comparison with the upper continental crust, International Journal of Earth Sciences, http://dx.doi.org/10.1007/s00531-00010-00635-x.

Hartmann, J., and N. Moosdorf (2011), Chemical weathering rates of silicate-dominated lithological classes and associated liberation rates of phosphorus on the Japanese Archipelago - implications for global scale analysis, Chemical Geology, http://dx.doi.org/10.1016/j.chemgeo.2010.1012.1004.

Hashimoto, S., N. Tanaka, T. Kume, N. Yoshifuji, N. Hotta, K. Tanaka, and M. Suzuki (2007), Seasonality of vertically partitioned soil CO_2 production in temperate and tropical forest Journal of Forest Research, 12(3), 209-221.

Hattori, T., S. Inanaga, H. Araki, P. An, S. Morita, M. Luxova, and A. Lux (2005), Application of silicon enhanced drought tolerance in Sorghum bicolor, Physiol Plantarum, 123(4), 459-466.

Hattori, T., K. Ishii, P. An, and S. Inanaga (2009), Growth Enhancement of Rye by Silicon Application Under Two Different Soil Water Regimes, J Plant Nutr, 32(2), 187-196.

Haug, T. A., R. A. Kleiv, and I. A. Munz (2010), Investigating dissolution of mechanically activated olivine for carbonation purposes, Applied Geochemistry, 25(10), 1547-1563.

Hegerl, G. C., and S. Solomon (2009), Risks of Climate Engineering, Science, 325(5943), 955-956.

Hernandez, M. A., and M. Torero (2011), Fertilizer Market Situation - Market Structure, Consumption and Trade Patterns, and Pricing Behavior, Discussion Paper series IFPRI, (1058), 76.

Hindar, A., R. F. Wright, P. Nilsen, T. Laessen, and R. Hogberget (2003), Effects on stream water chemistry and forest vitality after whole-catchment application of dolomite to a forest ecosystem in southern Norway, Forest Ecol Manag, 180(1-3), 509-525.

Hinsinger, P., O. N. Fernandes Barros, M. F. Benedetti, Y. Noack, and G. Callot (2001), Plant-induced weathering of a basaltic rock: experimental evidence, Geochimica et Cosmochimica Acta, 65(1), 137-152.

Hodgkinson, E. S., and C. R. Hughes (1999), The mineralogy and geochemistry of cement/rock reactions: high-resolution studies of experimental and analogue materials, Geological Society, London, Special Publications, 157(1), 195-211.

Honjo, S., S. J. Manganini, R. A. Krishfield, and R. Francois (2008), Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983, Prog Oceanogr, 76(3), 217-285.

Houghton, R. A. (2003), Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850-2000, Tellus B, 55(2), 378-390.

Huber, C., R. Baier, A. Gottlein, and W. Weis (2006), Changes in soil, seepage water and needle chemistry between 1984 and 2004 after liming an N-saturated Norway spruce stand at the Hoglwald, Germany, Forest Ecol Manag, 233(1), 11-20.

Hughes, H. J., F. Sondag, C. Cocquyt, A. Laraque, A. Pandi, L. Andre, and D. Cardinal (2011), Effect of seasonal biogenic silica variations on dissolved silicon fluxes and isotopic signatures in the Congo River, Limnol Oceanogr, 56(2), 551-561.

Huijgen, W. J. J., G. Witcamp, and R. Comans (2005), Mineral CO_2 sequestration by steel slag carbonation, Environmental Science and Technology, 39(24), 9676-9682.

Humborg, C., V. Ittekkot, A. Cociasu, and B. VonBodungen (1997), Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure, Nature, 386(6623), 385-388.

Humborg, C., D. J. Conley, L. Rahm, F. Wulff, A. Cociasu, and V. Ittekkot (2000), Silicon retention in river basins: Far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments, Ambio, 29(1), 45-50.

Huntzinger, D. N., J. S. Gierke, S. K. Kawatra, T. C. Eisele, and L. L. Sutter (2009), Carbon dioxide sequestration in cement kiln dust through mineral carbonation, Environmental Science & Technology, 43(6), 1986-1992.

Hyvonen, R., et al. (2007), The likely impact of elevated [CO(2)], nitrogen deposition, increased temperature and management on carbon sequestration in temperate and boreal forest ecosystems: a literature review, New Phytol, 173(3), 463-480.

Imrie, C. E., A. Korre, G. Munoz-Melendez, I. Thornton, and S. Durucan (2008), Application of factorial kriging analysis to the FOREGS European topsoil geochemistry database, Science of the Total Environment, 393(1), 96-110.

Institution of Mechanical Engineers (2009), Rail Freight: Getting on the right trackRep., Institution of Mechanical Engineers, London.

IPCC (2007), Climate Change 2007 - The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the IPCC, 1-996 pp.

Irvine, P. J., A. Ridgwell, and D. J. Lunt (2010), Assessing the regional disparities in geoengineering impacts, Geophys Res Lett, 37.

Irvine, P. J., A. Ridgwell, and D. J. Lunt (2011), Climatic effects of surface albedo geoengineering, J Geophys Res-Atmos, 116.

Ittekkot, V., C. Humborg, and P. Schafer (2000), Hydrological alterations and marine biogeochemistry: A silicate issue?, Bioscience, 50(9), 776-782.

Jin, X., N. Gruber, J. P. Dunne, J. L. Sarmiento, and R. A. Armstrong (2006), Diagnosing the contribution of phytoplankton functional groups to the production and export of particulate organic carbon, CaCO(3), and opal from global nutrient and alkalinity distributions, Global Biogeochemical Cycles, 20(2).

Jobbagy, E. G., and R. B. Jackson (2000), The vertical distribution of soil organic carbon and its relation to climate and vegetation, Ecol Appl, 10(2), 423-436.

Jones, D. L., P. G. Dennis, A. G. Owen, and P. A. W. van Hees (2003), Organic acid behavior in soils - misconceptions and knowledge gaps, Plant and Soil, 248(1-2), 31-41.

Jones, L. H. P., and K. A. Handreck (1967), Silica in soils, plants, and animals, Advances in Agronomy, 58, 107-149.

Jongmans, A. G., N. vanBreemen, U. Lundstrom, P. A. W. vanHees, R. D. Finlay, M. Srinivasan, T. Unestam, R. Giesler, P. A. Melkerud, and M. Olsson (1997), Rock-eating fungi, Nature, 389(6652), 682-683.

Joshi, M., E. Hawkins, R. Sutton, J. Lowe, and D. Frame (2011), Projections of when temperature change will exceed 2 degrees C above pre-industrial levels, Nat Clim Change, 1(8), 407-412.

Keeling, R. F., S. Piper, A. Bollenbacher, and J. Walker (2009), Atmospheric CO_2 records from sites in the SIO air sampling network, in Trends: A comendium of data on global change, edited, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., USA.

Keith, D. W. (2010), Photophoretic levitation of engineered aerosols for geoengineering, P Natl Acad Sci USA, 107(38), 16428-16431.

Keith, D. W., E. Parson, and M. G. Morgan (2010), Research on global sun block needed now, Nature, 463(7280), 426-427.

Kelemen, P. B., J. Matter, E. E. Streit, J. F. Rudge, W. B. Curry, and J. Blusztajn (2011), Rates and Mechanisms of Mineral Carbonation in Peridotite: Natural Processes and Recipes for Enhanced, in situ CO_2 Capture and Storage, Annual Review of Earth and Planetary Sciences, Vol 39, 39, 545-576.

Kempe, S., and E. T. Degens (1985), An Early Soda Ocean, Chemical Geology, 53(1-2), 95-108.

Kheshgi, H. S. (1995), Sequestering atmospheric carbon dioxide by increasing ocean alkalinity, Energy, 20(9), 915-922.

Köhler, P., J. Hartmann, and D. A. Wolf-Gladrow (2010), Geoengineering potential of artificially enhanced silicate weathering of olivine, P Natl Acad Sci USA, 107(47), 20228-20233.

Köhler, P., C. Völcker, J. Hauck, J. Abrams, D.A. Wolf-Gladrow (submitted) Geoengineering impact of open ocean dissolution of olivine on atmospheric CO_2, surface ocean pH and marine biology. Environmental Research Letters

Koltermann, K. P., V. Gouretski, and K. Jancke (2011), Hydrographic Atlas of the World Ocean Circulation Experiment (WOCE), edited by I. W. P. Office, Southampton.

Korndorfer, G. H., N. K. Savant, L. E. Datnoff, and G. H. Snyder (1999), Silicon nutrition and sugarcane production: A review, J Plant Nutr, 22(12), 1853-1903.

Kosednar-Legenstein, B., M. Dietzel, A. Leis, and K. Stingl (2008), Stable carbon and oxygen isotope investigation in historical lime mortar and plaster - Results from field and experimental study, Applied Geochemistry, 23(8), 2425-2437.

Koukouzas, N., V. Gemeni, and H. J. Ziock (2009), Sequestration of CO_2 in magnesium silicates, in Western Macedonia, Greece, International Journal of Mineral Processing, 93(2), 179-186.

Koukouzas, N. K., R. Zeng, V. Perdikatsis, W. Xu, and E. K. Kakaras (2006), Mineralogy and geochemistry of Greek and Chinese coal fly ash, Fuel, 85(16), 2301-2309.

Kreutzer, K. (1995), Effects of Forest Liming on Soil Processes, Plant and Soil, 168, 447-470.

Krevor, S., C. R. Graves, B. S. Van Gosen, and A. E. McCafferty (2009), Mapping the Mineral Resource Base for Mineral Carbon-Dioxide Sequestration in the Conterminous United StatesRep., USGS.

Lal, R., K. Lorenz, R. F. Hüttl, B. U. Schneider, and J. von Braun (2012), Recarbonization of the Biosphere, 559 pp., Springer, Heidelberg.

Lampitt, R. S., et al. (2008), Ocean fertilization: a potential means of geoengineering?, Philos T R Soc A, 366(1882), 3919-3945.

Laruelle, G. G., et al. (2009), Anthropogenic perturbations of the silicon cycle at the global scale: Key role of the land-ocean transition, Global Biogeochemical Cycles, 23.

Laruelle, G. G., H. H. Dürr, C. P. Slomp, and A. V. Borges (2010), Evaluation of sinks and sources of CO_2 in the global coastal ocean using a spatially-explicit typology of estuaries and continental shelves, Geophys Res Lett, 37.

Lasaga, A. C., J. M. Soler, J. Ganor, T. E. Burch, and K. L. Nagy (1994), Chemical-weathering rate laws and global geochemical cycles, Geochimica et Cosmochimica Acta, 58(10), 2361-2386.

Lasaga, A. C. (1995), Fundamental approaches in describing mineral dissolution and precipitation rates, Reviews in Mineralogy and Geochemistry, 31(1), 21-86.

Le Maitre, R. W. (1976), The Chemical Variability of some Common Igneous Rocks, Journal of Petrology, 17(4), 589-598.

Leake, J. R., A. L. Duran, K. E. Hardy, I. Johnson, D. J. Beerling, S. A. Banwart, and M. M. Smits (2008), Biological weathering in soil: the role of symbiotic root-associated fungi biosensing minerals and directing phiotosynthate-energy into grain-scale mineral weathering, Mineralogical Magazine, 72(1), 85-89.

Lee, S., and D. A. Spears (1997), Natural weathering of pulverized fuel ash and porewater evolution, Applied Geochemisrry, 12, 367-376.

Lenton, T. M., and N. E. Vaughan (2009), The radiative forcing potential of different climate geoengineering options, Atmos Chem Phys, 9(15), 5539-5561.

Leonardos, O. H., W. S. Fyfe, and B. I. Kronberg (1987), The use of ground rocks in laterite systems: An improvement to the use of conventional soluble fertilizers?, Chemical Geology, 60(1-4), 361-370.

Leonardos, O. H., S. H. Theodoro, and M. L. Assad (2000), Remineralization for sustainable agriculture: A tropical perspective from a Brazilian viewpoint, Nutrient Cycling in Agroecosystems, 56(1), 3-9.

Lowndes, I., and K. Jeffrey (2009), Optimising the efficiency of primary aggregate productionRep., 74 pp, Mineral Industry Research Organisation.

Ludwig, W., J. L. Probst, and S. Kempe (1996), Predicting the oceanic input of organic carbon by continental erosion, Global Biogeochemical Cycles, 10(1), 23-41.

Ludwig, W., P. Amiotte-Suchet, G. Munhoven, and J. L. Probst (1998), Atmospheric CO_2 consumption by continental erosion: present-day controls and implications for the last glacial maximum, Global and Planetary Change, 17, 107-120.

Ma, J. F., and E. Takahashi (1990), Effect of Silicon on the Growth and Phosphorus Uptake of Rice, Plant and Soil, 126(1), 115-119.

Ma, J. F. (2004), Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses, Soil Sci Plant Nutr, 50(1), 11-18.

Mackenzie, F. T., and R. M. Garrels (1966), Chemical mass balance between rivers and oceans, American Journal of Science, 264(7), 507-&.

Macleod, G., A. E. Fallick, and A. J. Hall (1991), The Mechanism of Carbonate Growth on Concrete Structures, as Elucidated by Carbon and Oxygen Isotope Analyses, Chemical Geology, 86(4), 335-343.

Maher, K. (2010), The dependence of chemical weathering rates on fluid residence time, Earth and Planetary Science Letters, 294, 101-110.

Manning, D. A. C. (2008), Biological enhancement of soil carbonate precipitation: passive removal of atmospheric CO_2, Mineralogical Magazine, 72, 639-649.

Manning, D. A. C. (2010), Mineral sources of potassium for plant nutrition. A review, Agron. Sustain. Dev., 30(2), 281-294.

Manning, D. A. C., and P. Renforth (2012), Passive sequestration of atmospheric CO_2 through coupled plant-mineral reactions, Environmental Science and Technology. doi: 10.1021/es301250j

Marland, G., T. Boden, and R. J. Andres (2005), Global Regional and National CO_2 Emissions, in Trends: A comendium of data on global change, edited, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., USA.

Martin, P., R. S. Lampitt, M. J. Perry, R. Sanders, C. Lee, and E. D'Asaro (2011), Export and mesopelagic particle flux during a North Atlantic spring diatom bloom, Deep-Sea Res Pt I, 58(4), 338-349.

Matichenkov, V. V., and E. A. Bocharnikova (2001), The relationship between silicon and soil physical and chemical properties, in Silicon in agriculture, edited, pp. 209-219, Elsevier, Amsterdam.

Max Planck Institute for Chemistry, M. (2006), Geochemistry of rocks of the oceans and continents, GEOROC, edited.

Mayes, W., P. Younger, and J. Aumônier (2008), Hydrogeochemistry of alkaline steel slag leachates in the UK, Water, Air, and Soil Pollution, 195(1), 35-50.

Mayes, W. M., A. R. G. Large, and P. L. Younger (2005), The impact of pumped water from a de-watered Magnesian limestone quarry on an adjacent wetland: Thrislington, County Durham, UK, Environ Pollut, 138(3), 443-454.

Mayes, W. M., P. L. Younger, and J. Aumonier (2006), Buffering of alkaline steel slag leachate across a natural wetland, Environmental Science & Technology, 40(4), 1237-1243.

Mayorga, E. (2008), Carbon cycle - Harvest of the century, Nature, 451(7177), 405-406.

Mayorga, E., S. P. Seitzinger, J. A. Harrison, E. Dumont, A. H. W. Beusen, A. F. Bouwman, B. M. Fekete, C. Kroeze, and G. Van Drecht (2010), Global Nutrient Export from WaterSheds 2 (NEWS 2): Model development and implementation, Environ Modell Softw, 25(7), 837-853.

McCarroll, D., and H. Viles (1995), Rock-weathering by the lichen Lecidea auriculata in an arctic alpine environment, Earth Surface Processes and Landforms, 20(3), 199-206.

McKinnon, A. C., and M. I. Piecyk (2009), Measurement of CO_2 emissions from road freight transport: A review of UK experience, Energy Policy, 37(10), 3733-3742.

McKinnon, A. C., and M. Piecyk (2010), Measuring and Managing CO_2 Emissions in European Chemical TransportRep., Cefic, Brussels.

Meinshausen et al. (2011), The RCP greenhouse gas concentrations and their extensions from 1765 to 2300, Climatic Change (2011) 109:213–241

Meunier, J. D., F. Colin, and C. Alarcon (1999), Biogenic silica storage in soils, Geology, 27(9), 835-838.

Meybeck, M. (1998), The IGBP water group: a resonse to a growing global concern, Global Change Newsletters, 36, 8-12.

Moore, J. C., S. Jevrejeva, and A. Grinsted (2010), Efficacy of geoengineering to limit 21st century sea-level rise, P Natl Acad Sci USA, 107(36), 15699-15703.

Moosdorf, N., J. Hartmann, R. Lauerwald, B. Hagedorn, and S. Kempe (2011), Atmospheric CO(2) consumption by chemical weathering in North America, Geochimica Et Cosmochimica Acta, 75(24), 7829-7854.

Morse, J. W., Q. W. Wang, and M. Y. Tsio (1997), Influences of temperature and Mg:Ca ratio on CaCO3 precipitates from seawater, Geology, 25(1), 85-87.

Morse, J. W., R. S. Arvidson, and A. Luttge (2007), Calcium carbonate formation and dissolution, Chem Rev, 107(2), 342-381.

Moulton, K. L., J. West, and R. A. Berner (2002), Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering, American Journal of Science, 300(7), 539-570.

Nakicenovic, N., and R. Swart (2000), Special report on emission scenarios, Cambridge University Press, Cambridge.

Nanayakkara, U. N., W. Uddin, and L. E. Datnoff (2008), Application of silicon sources increases silicon accumulation in perennial ryegrass turf on two soil types, Plant and Soil, 303(1-2), 83-94.

Nelson, D. M., P. Treguer, M. A. Brzezinski, A. Leynaert, and B. Queguiner (1995), Production and Dissolution of Biogenic Silica in the Ocean - Revised Global Estimates, Comparison with Regional Data and Relationship to Biogenic Sedimentation, Global Biogeochemical Cycles, 9(3), 359-372.

Nelson, D. M., and Q. Dortch (1996), Silicic acid depletion and silicon limitation in the plume of the Mississippi River: Evidence from kinetic studies in spring and summer, Mar Ecol-Prog Ser, 136(1-3), 163-178.

Nkouathio, D. G., P. Wandji, J. M. Bardintzeff, P. Tematio, A. Kagou Dongmo, and F. Tchoua (2008), Utilisation des roches volcaniques pour la reminéralisation des sols ferrallitiques des régions tropicales. Cas des pyroclastites basaltiques du graben de Tombel (Ligne volcanique du Cameroun), Bulletin de la Societe Vaudoise des Sciences Naturelles, 91, 1-14.

O'Halloran, T. L., et al. (2012), Radiative forcing of natural forest disturbances, Global Change Biol, 18(2), 555-565.

O'Connor, W. K., D. C. Dahlin, G. E. Rush, S. J. Gedermann, L. R. Penner, and D. N. Nilsen (2005), Aqueous mineral carbonation, Final Report - DOE/ARC-TR-04-002Rep.

Oelkers, E. H. (2001), General kinetic description of multioxide silicate mineral and glass dissolution, Geochimica Et Cosmochimica Acta, 65(21), 3703-3719.

Oelkers, E. H., and S. R. Gislason (2001), The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25 degrees C and pH=3 and 11, Geochimica Et Cosmochimica Acta, 65(21), 3671-3681.

Oelkers, E. H., S. R. Gislason, and J. Matter (2008), Mineral carbonation of CO_2, Elements, 4(5), 333-337.

Oh, N. H., and P. A. Raymond (2006), Contribution of agricultural liming to riverine bicarbonate export and CO_2 sequestration in the Ohio River basin, Global Biogeochemical Cycles, 20(3), GB3012.

Oschlies, A., M. Pahlow, A. Yool, and R. J. Matear (2010), Climate engineering by artificial ocean upwelling: Channelling the sorcerer's apprentice, Geophys Res Lett, 37.

Paces, T. (1983), Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments, Geochimica et Cosmochimica Acta, 47(11), 1855-1863.

Pagani, M., K. Caldeira, R. Berner, and D. J. Beerling (2009), The role of terrestrial plants in limiting atmospheric CO_2 decline over the past 24 million years, Nature, 460(7251), 85-88.

Palandri, J. L., and Y. K. Kharaka (2004), A complitation of rate parameters of water-mineral interaction kinetics for application to geochemical modellingRep., United States Geological Survey.

Parsons, M. B., D. K. Bird, M. T. Einaudi, and C. N. Alpers (2001), Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California, Applied Geochemistry, 16(14), 1567-1593.

Perrin, A. S., A. Probst, and J. L. Probst (2008), Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments: Implications for weathering CO_2 uptake at regional and global scales, Geochimica et Cosmochimica Acta, 72(13), 3105-3123.

Peters, G. P., G. Marland, C. Le Quere, T. Boden, J. G. Canadell, and M. R. Raupach (2012), CORRESPONDENCE: Rapid growth in CO_2 emissions after the 2008-2009 global financial crisis, Nat Clim Change, 2(1), 2-4.

Phillips, O. L., et al. (1998), Changes in the carbon balance of tropical forests: Evidence from long-term plots, Science, 282(5388), 439-442.

Pierson-Wickmann, A. C., L. Aquilina, C. Martin, L. Ruiz, J. Molenat, A. Jaffrezic, and C. Gascuel-Odoux (2009), High chemical weathering rates in first-order granitic catchments induced by agricultural stress, Chemical Geology, 265(3-4), 369-380.

Pokrovsky, O. S., and J. Schott (2000), Kinetics and mechanism of forsterite dissolution at 25C and pH from 1 to 12, Geochimica et Cosmochimica Acta, 64(19), 3313-3325.

Pongratz, J., D. B. Lobell, L. Cao, and K. Caldeira (2012), Crop yields in a geoengineered climate, Nat Clim Change, 2(2), 101-105.

Ragsdale, S. W. (2009), Nickel-based Enzyme Systems, Journal of Biological Chemistry, 284, 18571-18575.

Ragueneau, O., et al. (2000), A review of the Si cycle in the modem ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy, Global and Planetary Change, 26(4), 317-365.

Ragueneau, O., S. Schultes, K. Bidle, P. Claquin, and B. La Moriceau (2006), Si and C interactions in the world ocean: Importance of ecological processes and implications for the role of diatoms in the biological pump, Global Biogeochemical Cycles, 20(4).

Ragueneau, O., A. Regaudie-de-Gioux, B. Moriceau, M. Gallinari, A. Vangriesheim, F. Baurand, and A. Khripounoff (2009), A benthic Si mass balance on the Congo margin: Origin of the 4000 m DSi anomaly and implications for the transfer of Si from land to ocean, Deep-Sea Res Pt Ii, 56(23), 2197-2207.

Rawlins, C. H., K. D. Peaslee, and V. Richards (2008), Feasibility of processing steelmaking slag for carbon dioxide sequestration and metal recovery, Association for Iron & Steel Technology AIST.

Raymond, P. A., N.-H. Oh, R. E. Turner, and W. Broussard (2008), Anthropogenically enhanced fluxes of water and carbon from the Mississippi River, Nature, 451(7177), 449-452.

Renforth, P., D. A. C. Manning, and E. Lopez-Capel (2009), Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide, Applied Geochemistry, 24, 1757-1764.

Renforth, P., and D. A. C. Manning (2011), Laboratory carbonation of artificial silicate gels enhanced by citrate: implications for engineered pedogenic carbonate formation', Int J Greenh Gas Con, 5(6), 1578-1586.

Renforth, P., C. L. Washbourne, J. Taylder, and D. A. C. Manning (2011), Silicate Production and Availability for Mineral Carbonation, Environmental Science & Technology, 45(6), 2035-2041.

Renforth, P. (2012), The potential of enhanced weathering in the UK, Int J Greenh Gas Con. 10, 229-243

Ricke, K. L., G. Morgan, and M. R. Allen (2010), Regional climate response to solar-radiation management, Nature Geoscience, 3(8), 537-541.

Ricke, W. (1960), Ein Beitrag Zur Geochemie des Schwefels, Geochimica et Cosmochimica Acta, 21(1-2), 35-80.

Roadcap, G. S., W. B. Kelly, and C. M. Bethke (2005), Geochemistry of extremely alkaline (pH>12) ground water in slag fill aquifers Ground Water, 43(6), 806-816.

Robock, A., A. Marquardt, B. Kravitz, and G. Stenchikov (2009), Benefits, risks, and costs of stratospheric geoengineering, Geophys Res Lett, 36.

Robock, A., M. Bunzl, B. Kravitz, and G. L. Stenchikov (2010), A Test for Geoengineering?, Science, 327(5965), 530-531.

Rogelj, J., W. Hare, J. Lowe, D. P. van Vuuren, K. Riahi, B. Matthews, T. Hanaoka, K. J. Jiang, and M. Meinshausen (2011), Emission pathways consistent with a 2 degrees C global temperature limit, Nat Clim Change, 1(8), 413-418.

Rosenberg, D. M., P. McCully, and C. M. Pringle (2000), Global-scale environmental effects of hydrological alterations: Introduction, Bioscience, 50(9), 746-751.

Rosso, J. J., and J. D. Rimstidt (2000), A high resolution study of forsterite dissolution rates, Geochimica et Cosmochimica Acta, 64(5), 797-811.

Rost, B., I. Zondervan, and D. Wolf-Gladrow (2008), Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions, Mar Ecol-Prog Ser, 373, 227-237.

Roth, J. (1878), Flusswasser, Meerwasser, Steinsalz, 1-36 pp., Verlag von Carl Habel, Berlin.

Roth, J. (1879), Allgemeine und Chemische Geologie, Erster Band - Bildung und Umbildung der Mineralien. Quell-, Fluss- und Meerwasser. Die Abs„tze, 1-634 pp., Verlag von Wilhelm Hertz (Bessersche Buchhandlung), Berlin.

Roth, J. (1893), Allgemeine und Chemische Geologie, Dritter Band - Zweite Abteilung: Verwitterung, Zersetzung und Zerst”rung der Gesteine, 1-530 pp., Verlag von Wilhelm Hertz (Bessersche Buchhandlung), Berlin.

Rundle, S. D., N. S. Weatherley, and S. J. Ormerod (1995), The Effects of Catchment Liming on the Chemistry and Biology of Upland Welsh Streams - Testing Model Predictions, Freshwater Biol, 34(1), 165-175.

Ryskov, Y. G., V. A. Demkin, S. A. Oleynik, and E. A. Ryskova (2008), Dynamics of pedogenic carbonate for the last 5000 years and its role as a buffer reservoir for atmospheric carbon dioxide in soils of Russia, Global and Planetary Change, 61(1-2), 63-69.

Sarmiento, J. L., J. Simeon, A. Gnanadesikan, N. Gruber, R. M. Key, and R. Schlitzer (2007), Deep ocean biogeochemistry of silicic acid and nitrate, Global Biogeochemical Cycles, 21(1).

Savant, N. K., L. E. Datnoff, and G. H. Snyder (1997a), Depletion of plant-available silicon in soils: A possible cause of declining rice yields, Commun Soil Sci Plan, 28(13-14), 1245-1252.

Savant, N. K., G. H. Snyder, and L. E. Datnoff (1997b), Silicon management and sustainable rice production, Adv Agron, 58, 151-199.

Schopka, H.H., L.A. Derry, C.A. Arcilla (2011) Chemical weathering, river geochemistry and atmospheric carbon fluxes from volcanic and ultramafic regions on Luzon Island, the Philippines. Geochimica Et Cosmochimica Acta, 75(4), 978-1002.

Schuiling, R. D., and P. Krijgsman (2006), Enhanced weathering: An effective and cheap tool to sequester CO_2, Climatic Change, 74(1-3), 349-354.

Schuiling, R. D., and P. L. de Boer (2010), Coastal spreading of olivine to control atmospheric CO_2 concentrations: A critical analysis of viability. Comment: Nature and laboratory models are different, Int J Greenh Gas Con, 4(5), 855-856.

Schuiling, R. D., and P. L. de Boer (2011), Rolling stones; fast weathering of olivine in shallow seas for cost-effective CO_2 capture and mitigation of global warming and ocean acidification Earth System Dynamics Discussion, 2, 551-568.

Scrivener, K. L., T. Füllmann, E. Gallucci, G. Walenta, and E. Bermejo (2004), Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods, Cement and Concrete Research, 34(9), 1541-1547.

Semhi, K., P. A. Suchet, N. Clauer, and J. L. Probst (2000), Impact of nitrogen fertilizers on the natural weathering-erosion processes and fluvial transport in the Garonne basin, Applied Geochemistry, 15(6), 865-878.

Shaw, S., S. M. Clark, and C. M. B. Henderson (2000a), Hydrothermal formation of the calcium silicate hydrates, tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) and xonotlite ($Ca_6Si_6O_{17}(OH)_2$): an in situ synchrotron study, Chemical Geology, 167(1-2), 129-140.

Shaw, S., C. M. B. Henderson, and B. U. Komanschek (2000b), Dehydration/recrystallization mechanisms, energetics, and kinetics of hydrated calcium silicate minerals: an in situ TGA/DSC and synchrotron radiation SAXS/WAXS study, Chemical Geology, 167(1-2), 141-159.

Shipe, R. F., and M. A. Brzezinski (2001), A time series study of silica production and flux in an eastern boundary region: Santa Barbara Basin, California, Global Biogeochemical Cycles, 15(2), 517-531.

Shipe, R. F., J. Curtaz, A. Subramaniam, E. J. Carpenter, and D. G. Capone (2006), Diatom biomass and productivity in oceanic and plume-influenced waters of the western tropical Atlantic Ocean, Deep-Sea Res Pt I, 53(8), 1320-1334.

Sobanska, S., B. Ledésert, D. Deneele, and A. Laboudigue (2000), Alteration in soils of slag particles resulting from lead smelting, Comptes Rendus de l'Academie de Sciences - Serie IIa: Sciences de la Terre et des Planetes, 331(4), 271-278.

Solomon, S., G. K. Plattner, R. Knutti, and P. Friedlingstein (2009), Irreversible climate change due to carbon dioxide emissions, P Natl Acad Sci USA, 106(6), 1704-1709.

Sommer, M., D. Kaczorek, Y. Kuzyakov, and J. Breuer (2006), Silicon pools and fluxes in soils and landscapes - a review, Journal of Plant Nutrition and Soil Science, 169(3), 310-329.

Stallard, R. F., and J. M. Edmond (1983), Geochemistry of the Amazon .2. The Influence of Geology and Weathering Environment on the Dissolved-Load, J Geophys Res-Oc Atm, 88(Nc14), 9671-9688.

Stallard, R. F., and J. M. Edmond (1987), Geochemistry of the Amazon .3. Weathering Chemistry and Limits to Dissolved Inputs, J Geophys Res-Oceans, 92(C8), 8293-8302.

Stamboliadis, E., O. Pantelaki, and E. Petrakis (2009), Surface area production during grinding, Minerals Engineering, 22(7-8), 587-592.

Street-Perrott, F. A., and P. A. Barker (2008), Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon, Earth Surface Processes and Landforms, 33(9), 1436-1457.

Taylor, L. L., J. R. Leake, J. Quirk, K. Hardy, S. A. Banwart, and D. J. Beerling (2009), Biological weathering and the long-term carbon cycle: integrating mycorrhizal evolution and function into the current paradigm, Geobiology, 7(2), 171-191.

Taylor, S. R. (1964), Abundance of Chemical Elements in the Continental Crust - A New Table, Geochimica et Cosmochimica Acta, 28(AUG), 1273-1285.

ten Berge, H. F. M., H. G. van der Meer, J. W. Steenhuizen, P. W. Goedhart, P. Knops, and J. Verhagen (2012), Olivine Weathering in Soil, and Its Effects on Growth and Nutrient Uptake in Ryegrass (*Lolium perenne* L.): A Pot Experiment, PLoS ONE, 7(8), e42098.

Treguer, P., D. M. Nelson, A. J. Vanbennekom, D. J. Demaster, A. Leynaert, and B. Queguiner (1995), The Silica Balance in the World Ocean - a Reestimate, Science, 268(5209), 375-379.

Treguer, P., and C. L. De La Rocha (in press), The world ocean silica cycle, Annu Rev Mar Sci. 5,

Tripler, C. E., S. S. Kaushal, G. E. Likens, and M. T. Walter (2006), Patterns in potassium dynamics in forest ecosystems, Ecology Letters, 9(4), 451-466.

Turner, J. T. (2002), Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms, Aquat Microb Ecol, 27(1), 57-102.

Turner, R. E., and N. N. Rabalais (1994), Coastal Eutrophication near the Mississippi River Delta, Nature, 368(6472), 619-621.

UK-Royal-Society (2009), Geoengineering the climate: science, governance and uncertainty, The Royal Society, London, UK.

UNCTAD (2011), Review of maritime transport, 233, www.unctad.org/en/Docs/rmt2011_en.pdf,URLdoi.

Van Breemen, N., R. Finlay, U. Lundstrom, A. G. Jongmans, R. Giesler, and M. Olsson (2000), Mycorrhizal weathering: A true case of mineral plant nutrition ?, Biogeochemistry, 49(1), 53-67.

van Straaten, P. (2002), Rocks for Crops: Agrominerals of sub-Saharan Africa, 338 pp., ICRAF, Nairobi, Kenya.

VanCappellen, P., and L. Q. Qiu (1997a), Biogenic silica dissolution in sediments of the Southern Ocean .2. Kinetics, Deep-Sea Res Pt Ii, 44(5), 1129-1149.

VanCappellen, P., and L. Q. Qiu (1997b), Biogenic silica dissolution in sediments of the Southern Ocean .1. Solubility, Deep-Sea Res Pt Ii, 44(5), 1109-1128.

Volk, T., and M. I. Hoffert (1985), Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO_2 changes, in The Carbon Cycle and Atmospheric CO_2: Natural Variations - Archean to Present, in Geophysical Monographie Series, edited by E. T. Sundquist and W. S. Broecker, pp. 99-110, AGU, Washington.

Von Fragstein, P., W. Pertl, and H. Vogtmann (1988), Artificial weathering of silicate rock powders, Z Pflanzenernaehr Bodenk, 151, 141-146.

Vondamm, K. L., J. M. Edmond, B. Grant, and C. I. Measures (1985), Chemistry of Submarine Hydrothermal Solutions at 21-Degrees-N, East Pacific Rise, Geochimica Et Cosmochimica Acta, 49(11), 2197-2220.

Vorosmarty, C. J., and D. Sahagian (2000), Anthropogenic disturbance of the terrestrial water cycle, Bioscience, 50(9), 753-765.

Walker, J., P. B. Hays, and J. F. Kasting (1981), A negative feedback mechanism for the long-term stabilization of Earth's surface temperature, Journal of Geophysical Research, 86(C10), 9776-9782.

Walthall, J. H., and B. G.L. (1943), Fertilizer by Fusion of Rock Phosphate with Olivine, Industrial & Engineering Chemistry Research, 35(7), 774-777.

Wang, J., and N. Naser (1994), Improved Performance of Carbon-Paste Amperometric Biosensors through the Incorporation of Fumed Silica, Electroanal, 6(7), 571-575.

Wang, Y., and E. Forssberg (2003), International overview and outlook on comminution technologyRep., Lulea Tekniska Universitet: Avdelningen for Mineralteknik.

West, A. J., A. Galy, and M. Bickle (2005), Tectonic and climatic controls on silicate weathering, Earth and Planetary Science Letters, 235(1-2), 211-228.

Wheat, C. G., and M. J. Mottl (2000), Composition of pore and spring waters from Baby Bare: Global implications of geochemical fluxes from a ridge flank hydrothermal system, Geochimica Et Cosmochimica Acta, 64(4), 629-642.

White, A. F., and A. E. Blum (1995), Effects of Climate on Chemical-Weathering in Watersheds, Geochimica et Cosmochimica Acta, 59(9), 1729-1747.

Wilding, L. P., and L. R. Drees (1974), Contributions of forest opal and associated crystalline phases to fine silt and clay fractions of soils, Clays and Clay Minerals, 22, 295-306.

Wilson, S. A., G. M. Dipple, I. A. Power, J. M. Thom, R. G. Anderson, M. Raudsepp, J. E. Gabites, and G. Southam (2009), Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: examples from the Clinton Creek and Cassiar Chrysotile deposits, Canada, Econ. Geol., 104(1), 95-112.

Wilson, S. A., S. L. L. Barker, G. M. Dipple, and V. Atudorei (2010), Isotopic Disequilibrium during Uptake of Atmospheric CO_2 into Mine Process Waters: Implications for CO_2 Sequestration, Environmental Science & Technology, 44(24), 9522-9529.

Wilson, S. A., R. D. Schuiling, and I. M. Power (2011), Enhanced silicate weathering is not limited by silicic acid saturation, P Natl Acad Sci USA, 108(12), E41-E41.

Wogelius, R. A., and J. V. Walther (1991), Olivine dissolution at 25C: Effects of pH, CO_2, and organic acids, Geochimica et Cosmochimica Acta, 55(4), 943-954.

Wolf-Gladrow, D. A., R. E. Zeebe, C. Klaas, A. Kortzinger, and A. G. Dickson (2007), Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, Mar Chem, 106(1-2), 287-300.

Woods, S., C. J. Mitchell, D. J. Harrison, N. Ghazireh, and D. A. C. Manning (2004), Exploitation and use of quarry fines: a preliminary report, International Journal of Pavement Engineering and Asphalt Technology, 5, 54-62.

Yoshida, S., Y. Ohuishi, and K. Kitagishi (1962), Chemical forms, mobility and deposition of silicon in rice plant, Soil Science & Plants and Nutrient, 8, 107-113.

Zeebe, R. E., and D. Wolf-Gladrow (2001), CO_2 in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier Science Publishing, Amsterdam.

Zeebe, R. E., and K. Caldeira (2008), Close mass balance of long-term carbon fluxes from ice-core CO_2 and ocean chemistry records, Nature Geoscience, 1(5), 312-315.

Zwieniecki, M. A., P. J. Melcher, and N. M. Holbrook (2001), Hydrogel control of xylem hydraulic resistance in plants, Science, 291(5506), 1059-1062.

Figure captions:

Figure 1: Simplified equations describing reactions for the dissolution of simple carbonate and silicate minerals by different acids, illustrating the "consumption" of CO_2 during weathering by carbonic acid, as well as the contrasting role of strong acids such as HNO_3, which may derive from the application of nitrogen fertilizers. Carbonate weathering by nitric acid can be a net source of CO_2 to the atmosphere [after: *Hartmann and Kempe*, 2008]

Figure 2: Simplified schematic of the global C and Si cycle. Carbon land-atmosphere emissions (fossil fuels and deforestation: 10±0.9 Gt C a^{-1}), net ocean carbon uptake (2.4±0.5 Gt C a^{-1}) and land uptake by terrestrial ecosystems (2.6±1.0 Gt C a^{-1}) [*Peters et al.*, 2012]. The lateral land-ocean carbon fluxes are adapted from Ludwig et al. [1996; 1998] and IPCC [2007], estimates for emissions from inland waters (ranging from 1.2 to 3.2 Gt C a^{-1}) are from Aufdenkampe et al. [2011], and emissions occurring in the land-ocean transition zone from Laruelle et al. [2010]. Note that the emissions of CO_2 from limnic aquatic systems and the land-ocean transition zone are still poorly constrained and are not recognized in current Earth System models [c.f. the budget apporaches in: *Aufdenkampe et al.*, 2011; *IPCC*, 2007; *Peters et al.*, 2012]. Values for the silicon cycle are compiled after Dürr et al. [2011].

Figure 3: The Goldich dissolution series, adapted from Goldich [1938], showing the variation in dissolution rates for different minerals. Rate constants in italics are from Palandri and Kharaka [2004] at 25°C in mol cm^{-2} sec^{-1} (pH 4-6); artificial silicate weathering rates are reported in Renforth and Manning [2009].

Figure 4: Map showing identified sources of rocks with mafic minerals, like basalt or gabbro, for the American continents.

Figure 5: The "carbon consumption efficiency" of olivine weathering, updated from Köhler et al. [2010]. (A) Amount of olivine necessary for given CO_2 sequestration; less olivine would be needed at higher CO_2 partial pressures in the atmosphere, due to the chemical speciation of the carbonate system (according to Equations 1 to 7). (B) Sequestration ratio CO_2 to dissolved olivine (Pg:Pg), which

decreases with the amount of CO_2 sequestered from the atmosphere. Calculations are based on a well mixed 100 m deep surface ocean in equilibrium with the atmosphere. Theoretical limit (red line) follows the net Equation (Eq 8) of olivine dissolution without consideration of carbon cycle feedbacks.

Figure 6a: Dependence of olivine dissolution on pH [data from: *Golubev and Pokrovsky*, 2006; *Pokrovsky and Schott*, 2000; *Rosso and Rimstidt*, 2000; *Wogelius and Walther*, 1991]. Scatter in the data partly reflects variability in experimental designs, including different proportions of Mg and Fe in the olivine used in each experiment (note that rates in this plot are normalized to surface area of the minerals). The abiotic kinetics illustrated here suggest that dissolution rate, and thus the total amount of olivine dissolution that can be expected from an Enhanced Weathering scheme, may be pH-limited (compare with the discussion about kinetic limitations in section 2.3). Biotic processes (discussed in section 5) may increase the amount of potential dissolution, for several reasons. One of these is acidity; low pH-values of 4 to 6 are most common in soil systems, such that dissolution rates are expected to be faster in this setting compared to other natural environments (note the log-scale).

6b: Dissolution rates from a range of minerals, showing the large variability between minerals (and in some cases the same mineral) from a number of studies [*Palandri and Kharaka*, 2004 and references therein].

Figure 7: Modeling results that simulate the consequences of olivine dissolution with the BICYCLE-model, a box-model for the global carbon cycle [*Köhler et al.*, 2010]. (A) The sum of anthropogenic emissions from fossil fuel combustion (1750-2000 AD) [*Marland et al.*, 2005] and land use change (1850-2000 AD; before 1850 AD: linear extrapolation of land use change to zero in 1750 AD) [*Houghton*, 2003]. For 2000-2100 AD, the A2 emission scenario is used [*Nakicenovic and Swart*, 2000]. (B) Global atmospheric CO_2, including past data from the Law Dome ice core [*Etheridge et al.*, 1996] and instrumental measurements on Mauna Loa for 1958-2008 AD [*Keeling et al.*, 2009]. Forward simulation results of the A2 emission scenarios are shown with passive (constant) terrestrial carbon storage. The grey area covers the range of results from coupled carbon cycle-climate

simulations for the A2 emission scenario C^4MIP [*Friedlingstein et al.*, 2006]. (D) Impact of enhanced olivine dissolution for 2010-2060 AD on pCO_2 showing differences of simulated atmospheric pCO_2 versus the A2 emission baseline ($\Delta pCO_2=0$) for three different weathering scenarios (3 or 15 Gt olivine per year dissolved on land or in the open ocean, as shown in legend). Olivine dissolution on land implies the extraction of CO_2 out of the atmosphere and the riverine input of bicarbonate into the surface ocean following Eq. 8, while in the open ocean dissolution case only an input of alkalinity into the surface ocean is generated, which changes the marine carbonate system such that CO_2 is taken up by the ocean and pH is increased. The theoretical upper CO_2 sequestration limit is indicated by gray lines in D. This limit ignores the effects of the carbonate chemistry on the olivine dissolution and uses only the net dissolution Equation (Eq. 8), which implies that 1 mol of olivine introduces 4 moles of TA and DIC into the ocean. (C, E): Mean pH of the global surface ocean for the same scenarios as in B and D, respectively. The grey box in B,C covers years 2010-2060 AD, which are in focus in D and E. Further information can be found in Köhler et al. [2010].

Figure 8: (Left) A ‘hardpan’ of carbonate formed on waste slag mounds at former steelworks in Consett, United Kingdom. (Right) carbonate precipitation in waters egressing from a waste landfill in Scunthorpe steelworks (photograph courtesy of Carla-Leanne Washbourne). In both cases, rainwater has percolated through the material (dissolving Ca^{2+} and Mg^{2+}) and contact with DIC promotes the precipitation of carbonate.

Figure 9a: Areas with soils of low cation content or high groundwater table and/or where the hydrologically active surface is disconnected from rock material with significant amounts of elements (Ca, Mg, K, Na) available for cation-weathering and thus CO_2-consumption. These soil types cause a shielding effect for natural chemical weathering if compared to rock surfaces in direct contact with surface hydrological processes, as for example in steep, tectonically active areas with high physical erosion rates [*Hartmann et al.*, 2010a]. These locations are well suited for applying minerals to soils for Enhanced Weathering. Soil types distinguished here are gleysols, histosols, ferrasols and other deeply weathered soil types identified in the Harmonized World Soil Data Base [*FAO et al.*, 2008].

Figure 9b: Land cover distribution showing the boundaries of tropical regions [based on data from *Bartholome and Belward*, 2005].

Figure 10: Crushing energy (kWh t^{-1}) against generated surface area [adapted from *Axelson and Piret*, 1950; *Baláž et al.*, 2008; *Haug et al.*, 2010; *Stamboliadis et al.*, 2009]. There is relatively little data for the intermediate-energy grinding (0.1-5 m^2 g^{-1} surface area) and additional studies in this range would be a particular benefit to assessing Enhanced Weathering efficiencies. It is also possible to further increase dissolution rates with 'mechanochemical' activation, in which the silicate framework at the surface of the mineral is altered chemically [*Baláž et al.*, 2008; *Haug et al.*, 2010]. However, the energy requirements associated with mechanochemical activation are likely to limit the feasibility for Enhanced Weathering.

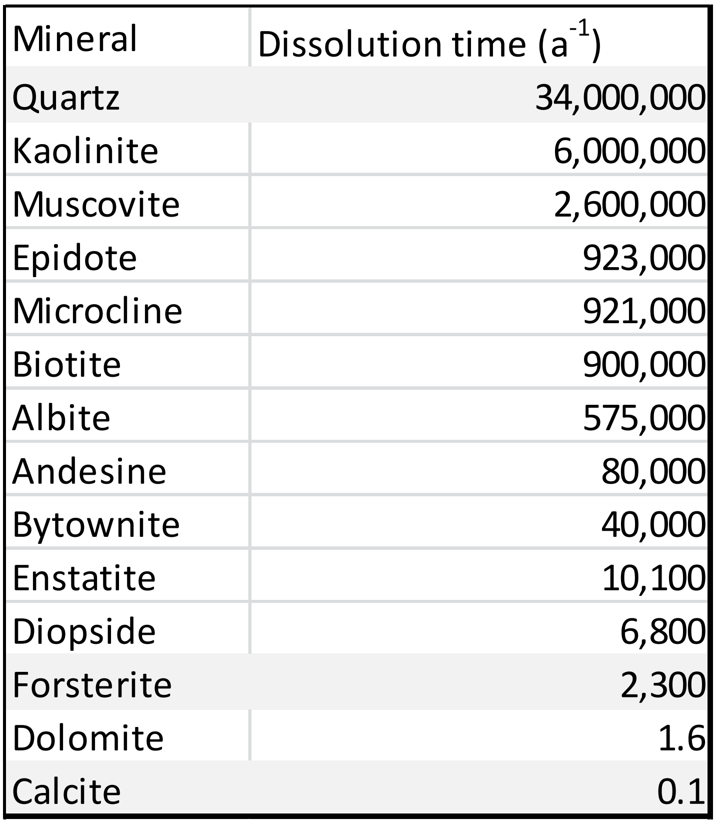
Figure 11: A broad conceptualisation of organic carbon and inorganic CO_2 dynamics in the environment. Organic carbon in the soil solution (as low molecular weight organic acids) which is exuded by soil flora and fauna contribute substantially to weathering of soil particles. Adapted from [*Jones et al.*, 2003].

Figure 12: Silicon is transferred within the terrestrial system as indicated by this figure, adapted from Cornelis et al. (2011) (Figure courtesy of Jean-Thomas Cornelis). The compartments of the biogeochemical Si cycle on continents were modified from Basile-Doelsch et al. [2005]. Solid line: transport; dashed line: dissolution; small dotted line: neoformation/precipitation; pointed-dotted line: adsorption/desorption. Numbers on arrows show inter-pool Si transfers in 10^{12} kg Si a^{-1} [*Matichenkov and Bocharnikova*, 2001; *Treguer et al.*, 1995].

Figure 13: Catchments of basins contributing most of the dissolved silica fluxes to the coastal zones are located in regions favorable for the Enhanced Weathering procedure. Specifically in South East Asia a significant amount of additional dissolved silica would be most likely intercepted by closed or semi-enclosed regional seas [Figure from *Dürr et al.*, 2011].

Tables:

Table 1: Lifetime of a hypothetical 1 mm sphere in a solution at pH 5 in years for different minerals.



Mineral	Dissolution time (a^{-1})
Quartz	34,000,000
Kaolinite	6,000,000
Muscovite	2,600,000
Epidote	923,000
Microcline	921,000
Biotite	900,000
Albite	575,000
Andesine	80,000
Bytownite	40,000
Enstatite	10,100
Diopside	6,800
Forsterite	2,300
Dolomite	1.6
Calcite	0.1

Forsterite (Mg-Olivine) is one of the most abundant minerals at Earth, and in comparison to other silicate minerals it is relatively fast to dissolve at pH 5 [*Lasaga*, 1995; *Renforth et al.*, 2009].

Table 2: Summary of major unknowns about silicate mineral dissolution rates in the context of Enhanced Weathering

- Quantitative effect of the approach to saturation state on mineral dissolution rate (for olivine and other target minerals)
- Effect of plant uptake of Si (decreasing saturation state of fluids)
- Effect of soil processes such as secondary mineral formation, and downward transport of solutes (decreasing saturation state of fluids)
- Extent of displacement of applied minerals to depth in agricultural soils
- Distribution of acids in soil solutions with depth
- Effect of percolation of water through the soil column, and associated water residence time
- Potential ecosystem-scale feedbacks (e.g., fertilization of terrestrial biological productivity leading to intensification of hydrologic cycle?)
- Effect of soil moisture variability (e.g., drying and wetting)

Table 3: The geochemical composition of some igneous rocks.

Weight %	Peridotite (close to Lherzolite)	Gabbro	Granodiorite	Granite	Basalt	Andesite	Rhyolite
SiO_2	42.43	50.34	66.07	71.20	49.11	57.71	72.70
TiO_2	0.63	1.12	0.54	0.31	1.84	0.87	0.28
Al_2O_3	4.25	15.54	15.73	14.30	15.71	16.95	13.25
Fe_2O_3	3.62	3.02	1.38	1.21	3.78	3.26	1.48
FeO	6.61	7.65	2.73	1.64	7.12	4.02	1.11
MnO	0.41	0.12	0.08	0.05	0.20	0.14	0.06
MgO	31.37	7.62	1.74	0.71	6.72	3.32	0.39
CaO	5.07	9.62	3.83	1.84	9.45	6.76	1.14
Na_2O	0.49	2.40	3.75	3.67	2.90	3.47	3.54
K_2O	0.34	0.39	2.73	4.06	1.10	1.61	4.29
P_2O_5	0.10	0.93	0.18	0.12	0.35	0.21	0.07
CO_2	0.30	0.24	0.08	0.05	0.11	0.05	0.08
S	0.02	0.02	0.02	0.02	0.07	0.36	0.06
SO_3	0.02	0.02	0.02	0.01	0.09	0.04	0.01
H_2O+	4.24	0.86	1.04	0.77	1.38	1.17	1.41
C	0.02	0.02	0.02	0.03	0.01	0.02	0.02
Cl	0.07	0.07	0.07	0.02	0.07	0.05	0.11
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Compiled in Hartmann [2011] [data based on: *Le Maitre*, 1976; *Max Planck Institute for Chemistry*, 2006; *Ricke*, 1960; *Taylor*, 1964]. From the left to the right: mafic to felsic plutonic rocks (peridotite to granite) and volcanic rocks (mafic basalt in comparison to more felsic types of volcanics like rhyolite). For igneous as well as volcanic rocks the content of Ca and Mg decreases from the left to the right.

Table 4: *Typical energy requirements for various crushing technologies*.

Crushing and Grinding technology	Feed particle size (μm)	Product Particle Size (μm)	Capacity (th^{-1})	Energy Use ($kWht^{-1}$)
Roller mills	10^4-10^5 20-30	18-65 7-12	12-225 15-65	6.6-11.0 7.6-36.0
Centrifugal mills	11	1-2		150.0
Ball / stirred media mills	150	<37	0.1-35$^{\$}$	13.0-233.0 20-100*
Impact crushing	10^4-10^5	10^3-10^2	130-1780*	0.6-1.5*
Cone crushing	10^5	10^3-10^2	80-1050*	0.3-1.5*
Jaw crushing	10^5-10^6	10^3	60-1600*	1.0-1.4*

*Indicative values derived from Metso technical data sheets

$^{\$}$Indicative values derived from Kefid technical data sheets

Sources: Wang and Forssberg [2003]; Lowndes and Jeffrey [2009]; Fuerstenau and Abouzeid [2002]; O'Connor et al., [2005].

Table 5: Emissions from a range of freight transport.

Freight/Haulage transport method	**gCO2 emission/km-tonne***
Airfreight	602
Road heavy goods vehicle	62
Diesel rail	15
Electric rail	14
Inland waterways	31
Large tanker	7
Sources: McKinnon and Piecyk [2009]; Mckinnon and Piecyk McKinnon and Piecyk [2010], Institution of Mechanical Engineers [2009].	

Table 6: Summary of potential side effects of Enhanced Weathering (considering local conditions)

Possible beneficial side-effects

- Increasing pH of ocean waters, counter-acting CO_2-induced acidification
- Supply of Si to coastal oceans
    - May counter-act Si-limitation and decrease Harmful Algal Blooms
    - May act as “ocean fertilization” to enhance sequestration of atmospheric CO_2 through the organic carbon biological pump
- Supply of Si and other nutrients (principally Fe, Mn, P, K) to terrestrial ecosystems
    - May increase terrestrial productivity and lead to greater sequestration of CO_2 in terrestrial biomass
    - May increase crop production
    - May provide additional income for farmers through CO_2-certificate trading

Possible problematic side-effects

- Change in pH of soils and surface waters (streams, rivers, lakes), affecting terrestrial and aquatic ecosystems
- Change in Si concentration of surface waters, affecting ecosystems via altered nutrient ratios
- Release of trace metals associated with target minerals (particularly Ni, Cd)
- Generation of dust
- Socio-economic and socio-political consequences for agricultural communities of a new, large-scale industrial and financial enterprise
- Environmental costs of an up three orders of magnitude increase in olivine mining globally

Table 7: Key target research areas for progress in the science behind Enhanced Weathering

- Better understanding of representative dissolution rates and their controls (see Table 2 in section 3)
- Assessing effect on alkalinity and cation supply on processes controlling carbonate precipitation in coastal and oceanic water bodies
- Identification of key mineral resources and their distribution
- Optimizing techniques for grinding
- Understanding main potential side effects (see Table 6)
- Identifying and quantifying key large-scale feedbacks
    - influence of changing nutrient status on plant-weathering systems
    - changes in productivity of agricultural and terrestrial ecosystems, and effects on the hydrological cycle
    - Si and alkalinity fluxes to the oceans, and their effects (e.g., change in nutrient elemental ratios like N/Si or P/Si and altered proton fluxes (pH)
- Quantifying effects of enhanced alkalinity fluxes on the carbonate system in the coastal and open oceans
- Developing overall dose-response relationship quantifying the net “carbon consumption efficiency” of different scenarios of mineral application
- Developing techniques for being able to monitor mineral dissolution over large spatial scales accurately
- Developing effective monitoring strategies for local to regional alterations of biogeochemical fluxes, as part of building institutional structures for sustainable global management of material fluxes

Figure 1:

Typical mineral reactions

(**educts** ⇨ **ions in dissolution** ⇨ **typical precipitation reactions in the ocean**)

Carbonate (not a silicate)

$CaCO_3 + CO_2 + H_2O \Rightarrow Ca^{2+} + 2HCO_3^- \Rightarrow CaCO_3 \Downarrow + CO_2 \Uparrow + H_2O$

(No net-sink of consumed atmospheric CO_2)

Olivine

$Mg_2SiO_4 + 4CO_2 + 4H_2O \Rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4 \Rightarrow 2MgCO_3 \Downarrow + SiO_2 \Downarrow + 2CO_2 \Uparrow + 4\,H_2O$

(Net-sink for ~50% of consumed atmospheric CO_2)

Albite

$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4 \Rightarrow 2Na^+ + 2HCO_3^- + SiO_2 \Downarrow$

(Net-sink for < 100% of consumed atmospheric CO_2)

Influence of nitrogen fertilizers

K-feldspar (silicate)

$2KAlSi_3O_8 + 2CO_2 + 11H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_4$

$2KAlSi_3O_8 + CO_2 + HNO_3 + 10H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + HCO_3^- + NO_3^- + 4H_4SiO_4$

$2KAlSi_3O_8 + 2HNO_3 + 9H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2\,NO_3^- + 4H_4SiO_4$

Calcite (carbonate)

$CaCO_3 + CO_2 + H_2O \Rightarrow Ca^{2+} + 2HCO_3^-$

$CaCO_3 + HNO_3 + H_2O \Rightarrow Ca^{2+} + HCO_3^- + NO_3^-$

$CaCO_3 + \mathbf{2HNO_3} \Rightarrow Ca^{2+} + 2NO_3^- + \mathbf{CO_2} \Uparrow + H_2O$

Figure 2:

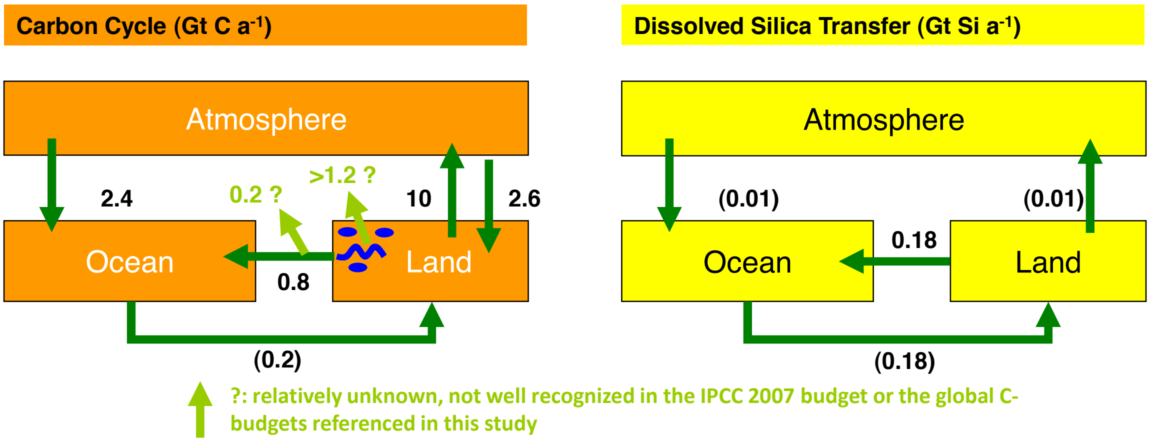

Carbon Cycle (Gt C a-1)
Atmosphere
Ocean
Land
2.4
0.2 ?
>1.2 ?
10
2.6
0.8
(0.2)
Dissolved Silica Transfer (Gt Si a-1)
Atmosphere
Ocean
Land
(0.01)
(0.01)
0.18
(0.18)
?: relatively unknown, not well recognized in the IPCC 2007 budget or the global C-budgets referenced in this study

Figure 3:

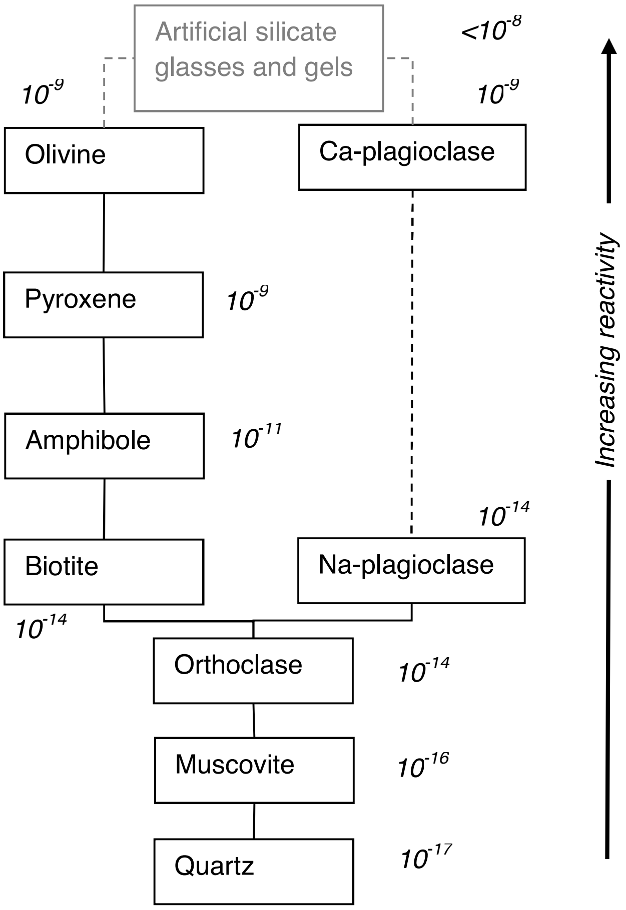
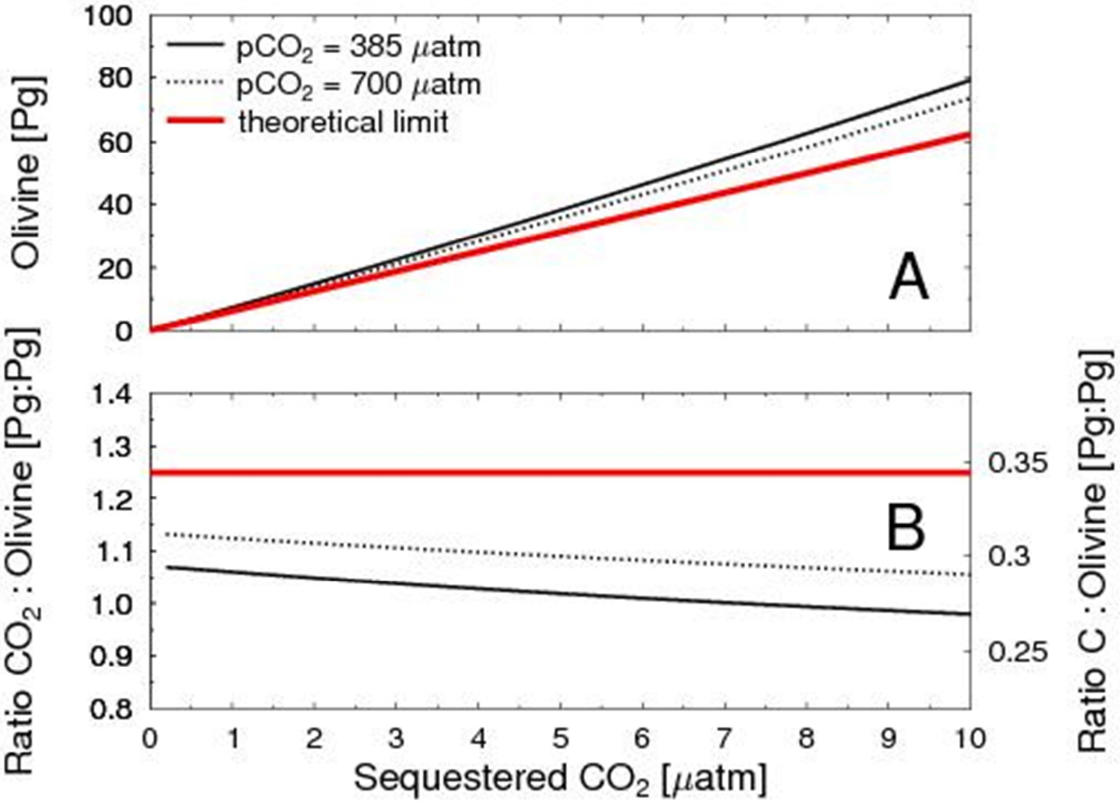

Artificial silicate glasses and gels
<10^-8
10^-9
10^-9
Olivine
Ca-plagioclase
Pyroxene
10^-9
Amphibole
10^-11
Increasing reactivity
10^-14
Biotite
Na-plagioclase
10^-14
Orthoclase
10^-14
Muscovite
10^-16
Quartz
10^-17

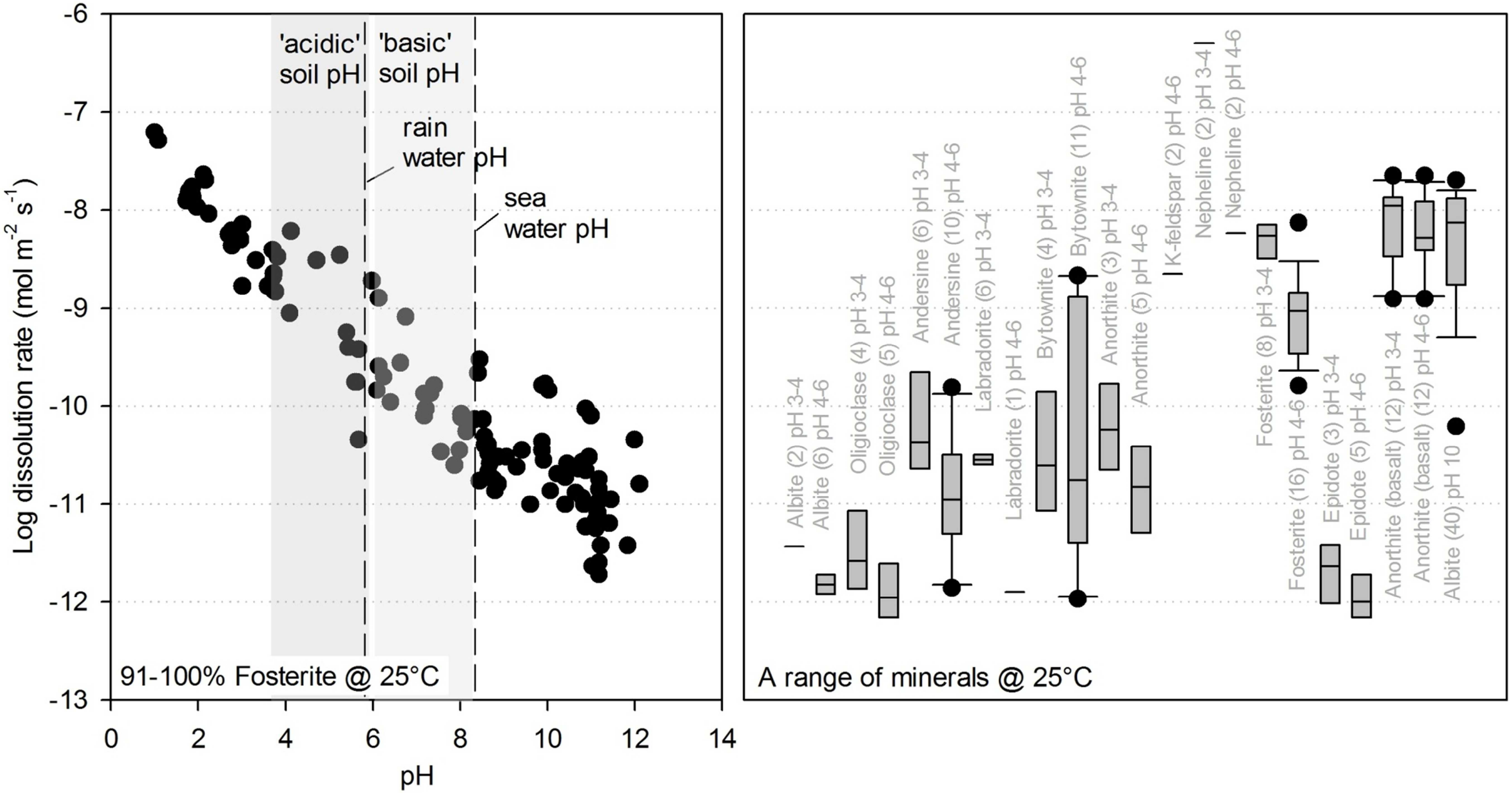
Figure 4:

Figure 5:



pCO$_2$ = 385 μatm
pCO$_2$ = 700 μatm
theoretical limit
Olivine [Pg]
100
80
60
40
20
0
A
Ratio CO$_2$: Olivine [Pg:Pg]
1.4
1.3
1.2
1.1
1.0
0.9
0.8
B
Ratio C : Olivine [Pg:Pg]
0.35
0.3
0.25
0
1
2
3
4
5
6
7
8
9
10
Sequestered CO$_2$ [μatm]

Figure 6:



-6
-7
-8
-9
-10
-11
-12
-13
Log dissolution rate (mol m^{-2} s^{-1})
0
2
4
6
8
10
12
14
pH
'acidic' soil pH
'basic' soil pH
rain water pH
sea water pH
91-100% Fosterite @ 25°C
A range of minerals @ 25°C
Albite (2) pH 3-4
Albite (6) pH 4-6
Oligioclase (4) pH 3-4
Oligioclase (5) pH 4-6
Andersine (6) pH 3-4
Andersine (10) pH 4-6
Labradorite (6) pH 3-4
Labradorite (1) pH 4-6
Bytownite (4) pH 3-4
Bytownite (11) pH 4-6
Anorthite (3) pH 3-4
Anorthite (5) pH 4-6
K-feldspar (2) pH 4-6
Nepheline (2) pH 3-4
Nepheline (2) pH 4-6
Fosterite (8) pH 3-4
Fosterite (16) pH 4-6
Epidote (3) pH 3-4
Epidote (5) pH 4-6
Anorthite (basalt) (12) pH 3-4
Anorthite (basalt) (12) pH 4-6
Albite (40) pH 10

Figure 7

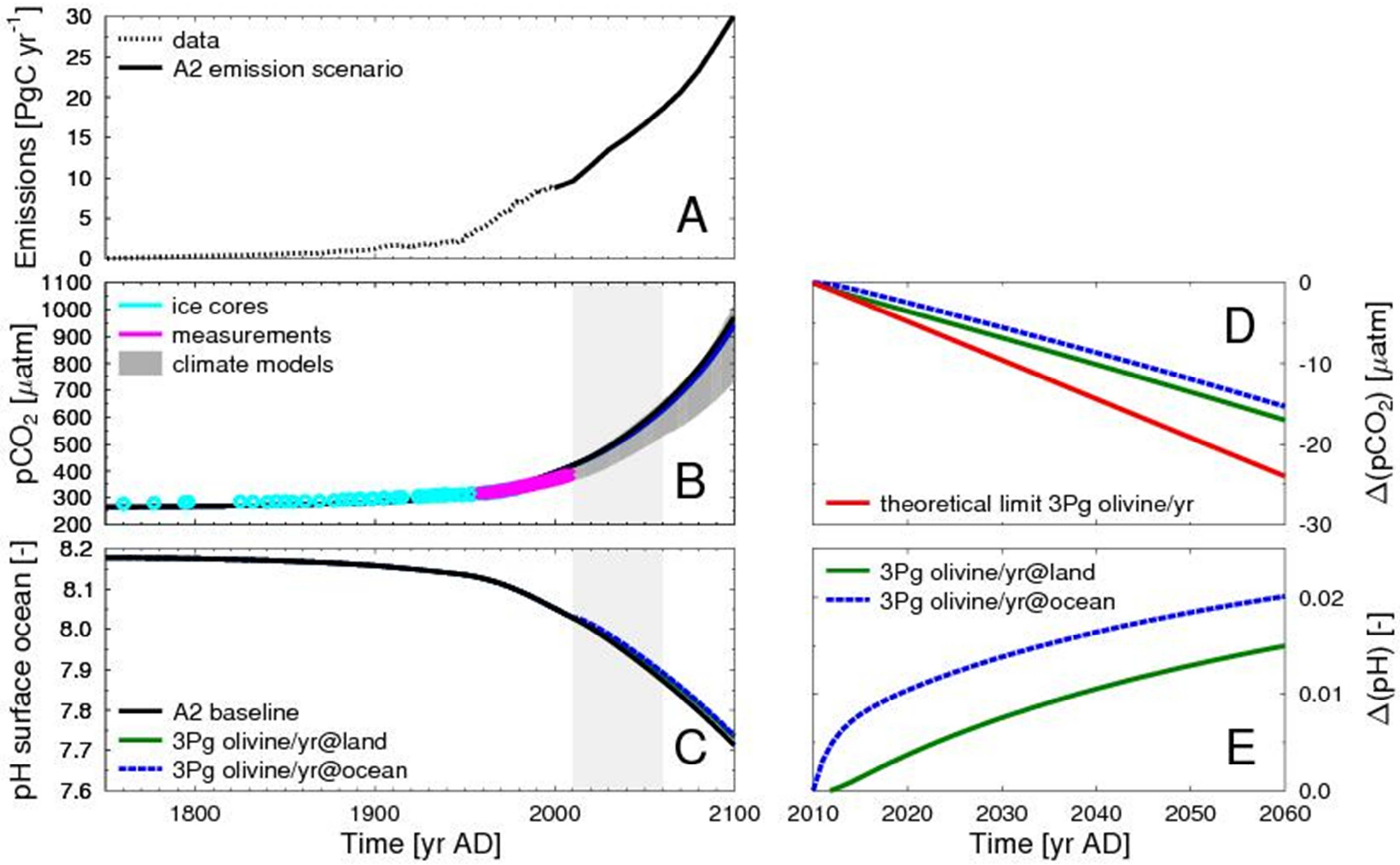

Emissions [PgC yr^{-1}]
data
A2 emission scenario
A
pCO$_2$ [μatm]
ice cores
measurements
climate models
B
pH surface ocean [-]
A2 baseline
3Pg olivine/yr@land
3Pg olivine/yr@ocean
C
D
theoretical limit 3Pg olivine/yr
Δ(pCO$_2$) [μatm]
E
3Pg olivine/yr@land
3Pg olivine/yr@ocean
Δ(pH) [-]
Time [yr AD]
Time [yr AD]
0
5
10
15
20
25
30
200
300
400
500
600
700
800
900
1000
1100
7.6
7.7
7.8
7.9
8.0
8.1
8.2
1800
1900
2000
2100
2010
2020
2030
2040
2050
2060
0
-10
-20
-30
0.0
0.01
0.02

Figure 8:

Figure 9a:

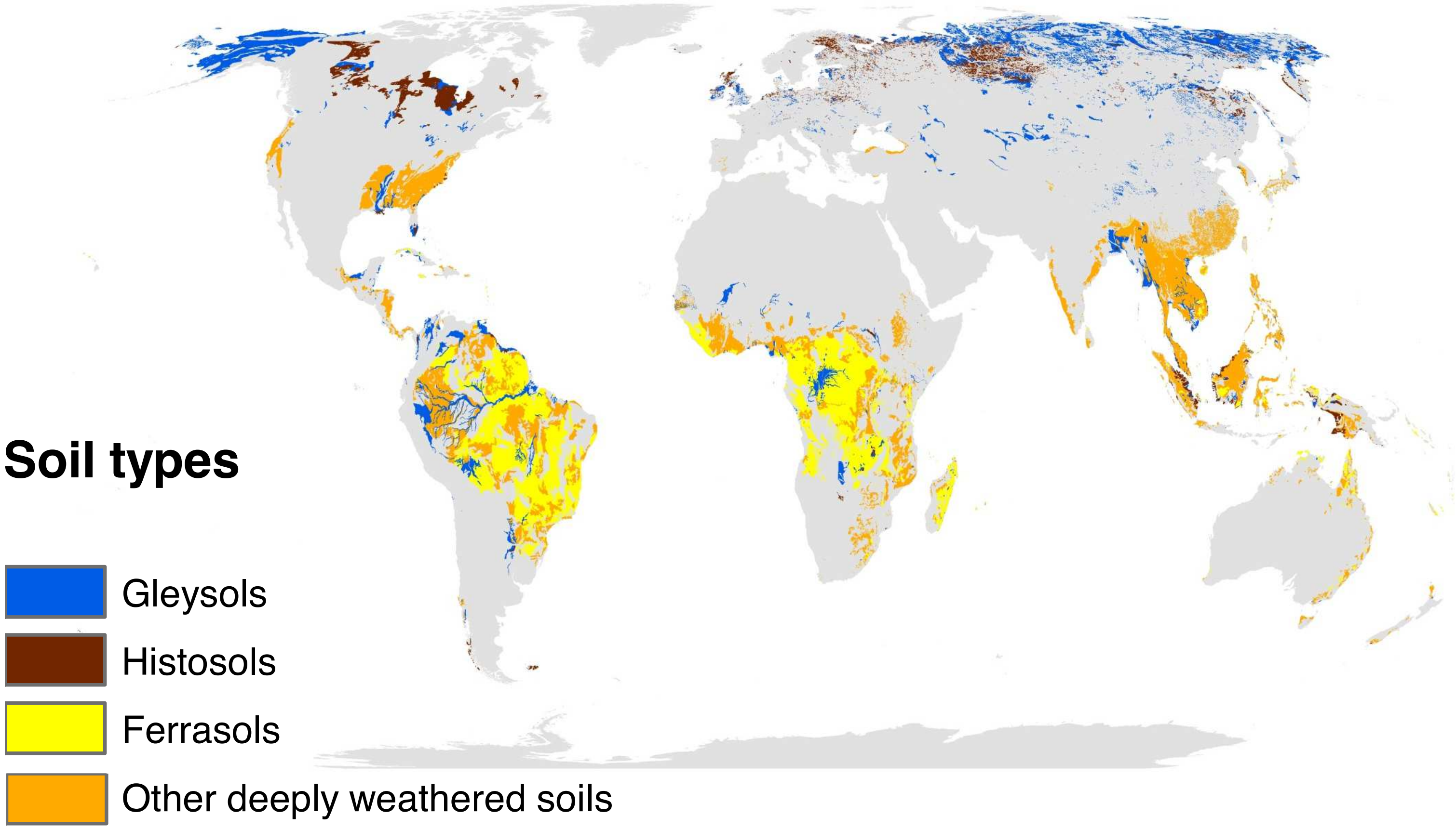

Soil types
Gleysols
Histosols
Ferrasols
Other deeply weathered soils

Figure 9b:

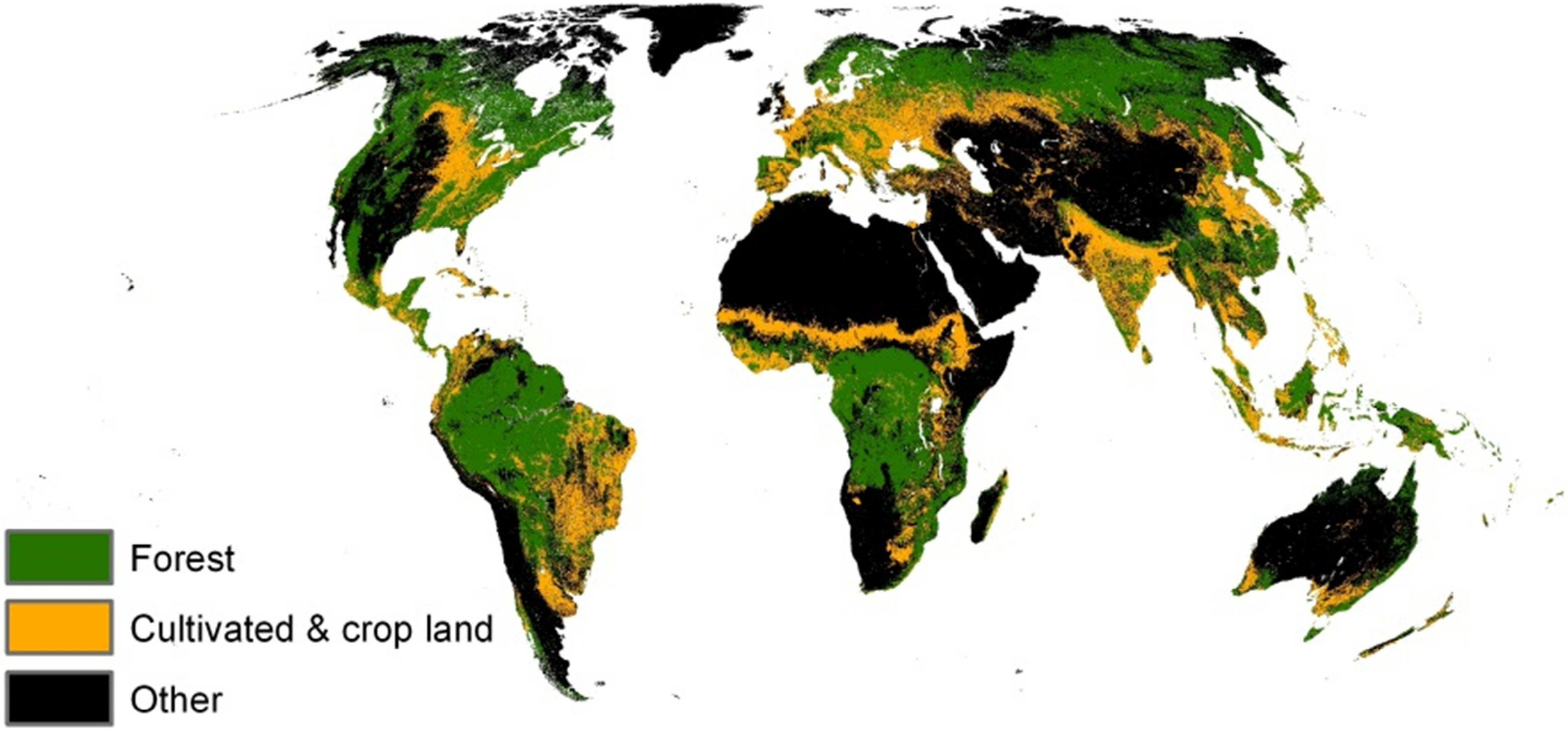
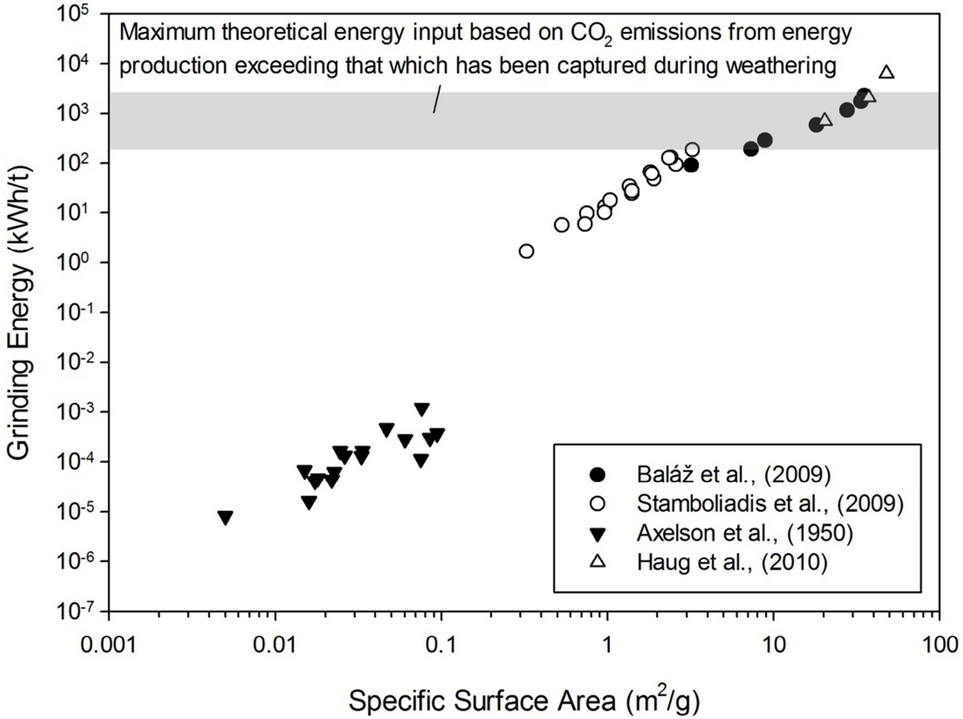


Figure 10:


Maximum theoretical energy input based on CO2 emissions from energy production exceeding that which has been captured during weathering
Grinding Energy (kWh/t)
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
0.001
0.01
0.1
1
10
100
Specific Surface Area (m2/g)
Baláž et al., (2009)
Stamboliadis et al., (2009)
Axelson et al., (1950)
Haug et al., (2010)

2118

Figure 11:

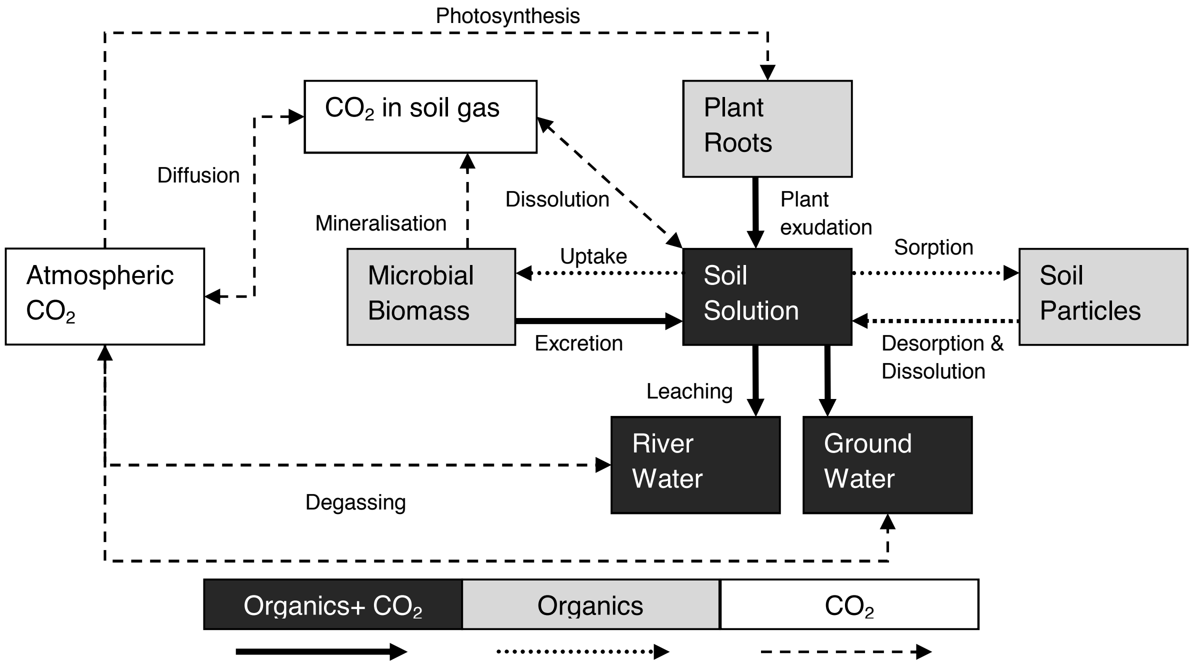
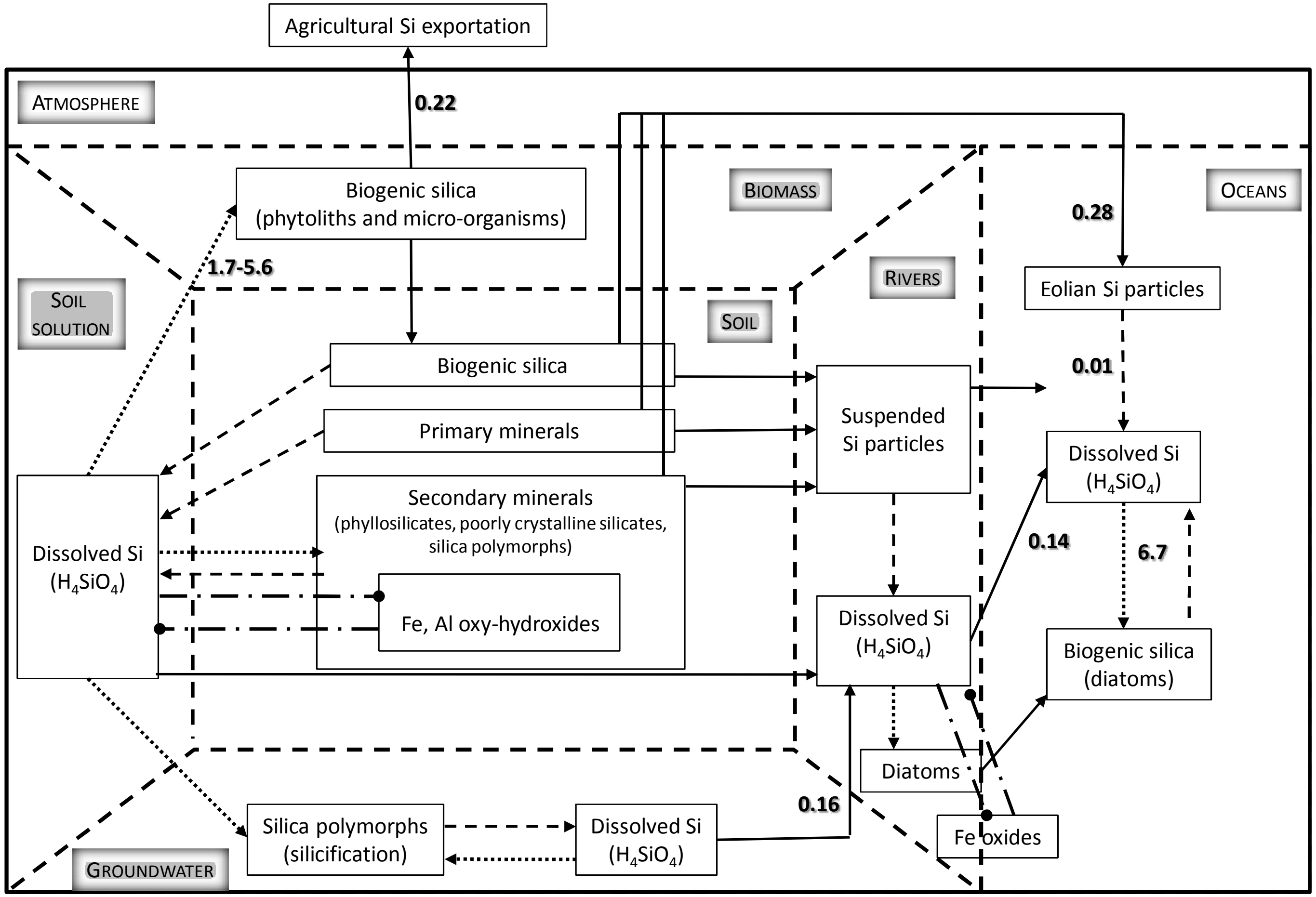
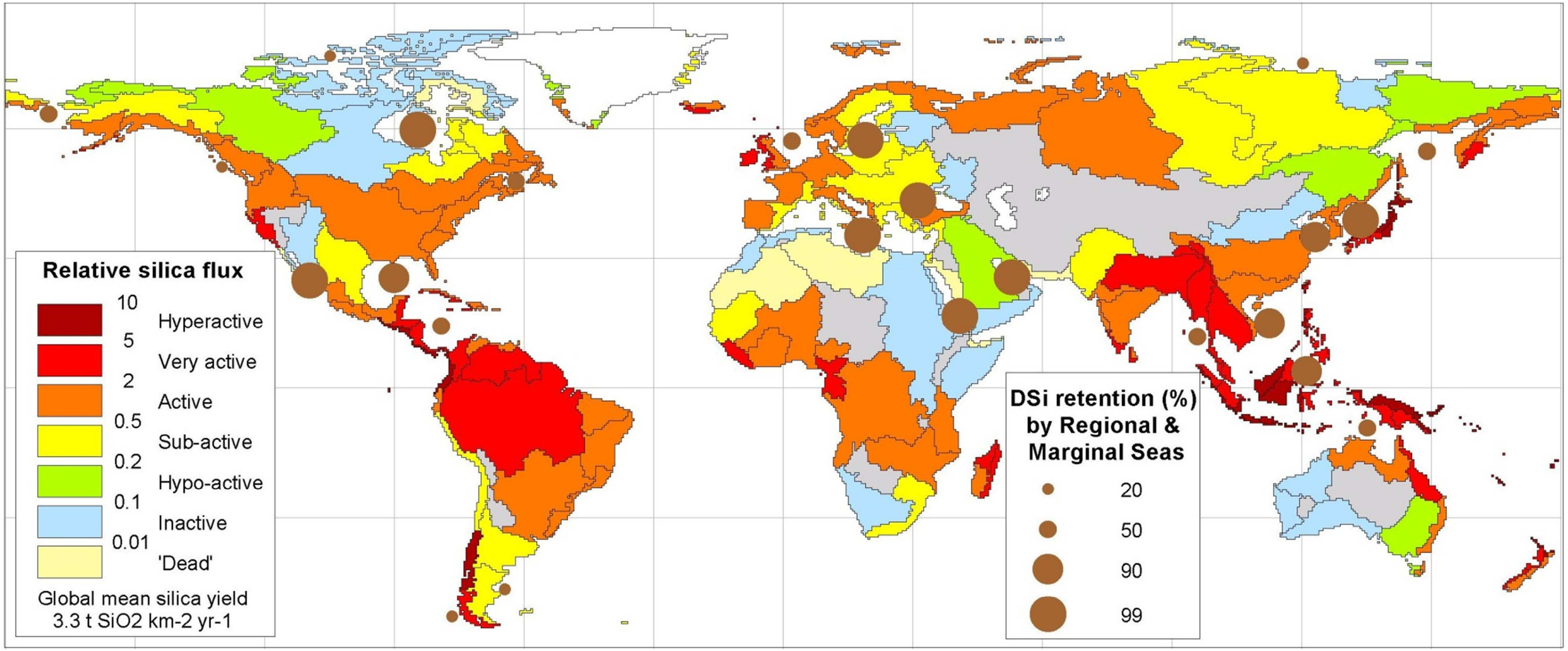

Photosynthesis
CO2 in soil gas
Plant Roots
Diffusion
Dissolution
Mineralisation
Plant exudation
Uptake
Sorption
Atmospheric CO2
Microbial Biomass
Soil Solution
Soil Particles
Excretion
Desorption & Dissolution
Leaching
River Water
Ground Water
Degassing
Organics+ CO2
Organics
CO2

Figure 12:



Agricultural Si exportation
0.22
ATMOSPHERE
BIOMASS
OCEANS
Biogenic silica
(phytoliths and micro-organisms)
0.28
1.7-5.6
RIVERS
Eolian Si particles
SOIL SOLUTION
SOIL
Biogenic silica
0.01
Suspended Si particles
Primary minerals
Dissolved Si (H_4SiO_4)
Secondary minerals
(phyllosilicates, poorly crystalline silicates, silica polymorphs)
0.14
6.7
Dissolved Si (H_4SiO_4)
Fe, Al oxy-hydroxides
Dissolved Si (H_4SiO_4)
Biogenic silica
(diatoms)
Diatoms
0.16
Fe oxides
Silica polymorphs
(silicification)
Dissolved Si (H_4SiO_4)
GROUNDWATER

Figure 13:


Relative silica flux
10
5
2
0.5
0.2
0.1
0.01
Hyperactive
Very active
Active
Sub-active
Hypo-active
Inactive
'Dead'
Global mean silica yield
3.3 t SiO2 km-2 yr-1
DSi retention (%)
by Regional &
Marginal Seas
20
50
90
99

.

2130

Enhanced Chemical Weathering as a Geoengineering Strategy to Reduce Atmospheric Carbon Dioxide, a Nutrient Source and to Mitigate Ocean Acidification

Supplement Information

1. Management of enhanced weathering at a geoengineering scale

To sequester a significant amount of carbon dioxide from the atmosphere, an Enhanced Weathering program would need to process 1 Gt to 10s of Gt of rock per year. This would make it one of the largest global industries. Therefore, as discussed in previous sections, it would require a well-organized assessment of altered biogeochemical fluxes as well as broader environmental and other consequences. In this case, attention is focused on analysing the various benefits, costs and risks of technologies and pathways, taking into account multiple criteria of evaluation, including environmental, agricultural, public health, and financial criteria as well as the projected magnitude of CO_2 sequestration. A comprehensive diagnostic process would develop a governance and accounting structure that includes local, regional and global stakeholders and decision makers, including mining corporations and the minerals transport industry, farmers and forest businesses, and the civil society and local stakeholders such as citizens in the vicinity of areas where Enhanced Weathering is employed. Later phases would require an agency organizing the global review and monitoring in light of data gathered from the various regions of application.

Stakeholder involvement in decision-making and management can be described as a multi-step process that includes the following phases (see Figure SI-1) [based on *Scheffran*, 2006]:

1. *Situation and context analysis:* To assist decision makers with proactive planning and management [c.f. *van Ast and Boot*, 2003], various methods from system dynamics and spatial modelling would be used to study the consequences of the application of Enhanced Weathering in time and space, at local and global levels. Much of the scientific analysis reviewed in this article falls into this analysis, including the CO_2-sequestration mechanisms and fluxes in the respective

natural systems. This analysis should also include consideration of relevant social and economic factors.

2. *Option identification and scenario generation:* In order to provide key information about the various possible options for implementation, computer simulations are needed to explore selected scenarios and identify the most relevant possibilities, and their consequences. These models need to be able to allow comparison of greenhouse gas reductions under different actions. Spatio-temporal analyses can determine the effectiveness of previous management decisions and provide projections for future management choices. Modelling the alteration of material fluxes due to Enhanced Weathering would demand a new generation of Earth System Models capable of forecasting consequences at the regional as well as at the global scale, learning from more advanced modelling approaches for solar radiation management (Kravitz et al. 2011, Schmidt et al 2012).

3. *Assessment of consequences and criteria-based evaluation:* A systemic approach is crucial for identifying the plausible causal chains and consequences which could result from the use of different Enhanced Weathering techniques in particular environments, including ecological impacts and other risks, as well as social effects including domestic protests and international conflicts. This analysis is based on the plausibility, relevance and uncertainty of events, building on principles, criteria and performance indicators defined by scientists, decision makers and other stakeholders (see, for example, the criteria given in the following section). Possible guardrails and critical limits could include thresholds for soil chemistry or water pH, or limitations on the addition of specific elements into local aquatic-, soil- or ecosystems-systems.

4. Decision-making and negotiation: Without agreement, disputes among interest groups could block decision-making and problem solving. Integrated Enhanced Weathering decision-making and risk management (building on the experience from disaster risk management strategies [e.g.,*Hartmann et al.*, 2006; *Levy et al.*, 2007; *Schneider*, 2008] can use various tools, including optimal control, multi-criteria methods, agent-based modeling and experimental games. Conflict resolution, participatory approaches and mediation can help to balance different interests.

5. *Planning and rules for action:* To implement actions on Enhanced Weathering, concrete planning is required, with specific rules and regulations that need to be followed and verified. In an environment with high uncertainties and rapidly changing conditions, planning needs to adapt to the state of knowledge and capability. For international coordination of regional processes, institutional mechanisms, governance structures and legal approaches are required that involve stakeholders [c.f. *Shidawara*, 1999]. One approach is to create incentives to participate and coordinate, e.g. through a global certification system and purposeful designed syndication of the Earth system [*Elliott and Hanson*, 2003]. Legal instruments can apply at national and multi-national levels to authorize or restrain certain Enhanced Weathering measures [UBA 2012].

6. Monitoring and learning: Continuous monitoring of the outcomes of global Enhanced Weathering application is critical for learning and improvement. Key indicators about anticipated consequences must be monitored, and the initial proposed environmental indicators need to be continuously re-evaluated. Existing environmental monitoring programs are restricted by the limited number of monitoring stations and need to be accompanied by comprehensive information sources, including land use and socio-economic data [c.f. *Plate*, 2002].

The information gathered throughout the monitoring and learning process can then be an input for further situation and context analysis (Step 1, above). These phases form a repeated cycle of multi-stakeholder participation, assessment and management (see Figure SI-1). As a result of learning and repetition, the assessment and management process can be made more effective. Connecting activities in this cycle are the extraction of essential information, the simulation of scenarios, the data-based validation of results, the evaluation of consequences, the communication of decisions and outcomes, and the capacity-building of involved actors. In each of these phases, particular stakeholders can participate according to their qualification, and various tools can be used for supporting the respective stages as well as the interaction of stakeholders throughout the process.

2. Legal framework and recent developments on climate engineering with relevance for Enhanced Weathering

Legal instruments to regulate Enhanced Weathering can apply at different levels. Individual states can promote a variety of national policies and regulations to authorize or prohibit certain Enhanced Weathering measures. In accordance with customary international law, states have to ensure that activities within their own territory do not generate substantial adverse consequences for the environment beyond their own borders. Substantial adverse effects on the environment are not permitted in areas such as the high seas, the Antarctic and outer space. At present, there are no effective geoengineering technologies, nore binding international regulations. The proposed geoengineering technique of Enhanced Weathering would also change global biogeochemical cycles, not only climate, and is at a smaller scale already in practice due the unregulated changes in land use or agricultural practices. While some treaties cover partial aspects, they would need to be extended to be effective [see the reviews in: *Proelss and Güssow*, 2011; *Rickels et al.*, 2011; *Umweltbundesamt*, 2011].

In particular, the UN Framework Convention on Climate Change (UNFCCC) precludes dangerous anthropogenic interference with the climate system, which would apply to dangerous climate change as well dangerous climate engineering. To be more binding, the term "dangerous interference" would have to be specified. Similarly, the 1978 Convention on the Prohibition of Military or Any Other Hostile Use of Environmental Modification Techniques (ENMOD) restrains the military or other hostile modification of the Earth's environment, but it does not prohibit the peaceful use of environmental modification. One example for which already some treaties could be applied is the proposed use of sulphur aerosols as a geoengineering technique [*Crutzen*, 2006]: Since the release of sulphur aerosols could damage the ozone layer, it could be contrary to the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer.

Research into ocean fertilization is basically allowed by regulations, if it is ensured that hazards for humans and the environment are avoided. Of particular relevance are the 1982 United Nations Convention on the Law of the Sea, the 1972 Convention on the Prevention of Marine Pollution through Dumping of Wastes and other Matter, and the corresponding London Protocol. These should equally apply to Enhanced Weathering, if minerals are to be spread near or along coastlines, or in the open ocean.

It remains to be decided whether there should be a standardized, broad regulation on geoengineering, or whether the respective international conventions should be supplemented with specific provisions on geoengineering measures such as Enhanced Weathering, e.g. within the UNFCCC. Regulatory questions pertain not just to the implementation of geoengineering, but also to research at the field scale. Political debates are gaining in importance, with first steps being taken in the US and Great Britain towards defined national research strategies and regulation requirements. The progressive development, including scientific research, of any geoengineering technology needs clear political regulation and coordination. This may come from a number of different directions:

- While the UNFCCC parties have not yet taken a stand on climate engineering, the Parties to the 2008 Convention on Biological Diversity (CDB) formulated a resolution whose content was virtually identical to that of the 2008 London Convention and London Protocol [*IMO*, 1996]. The tenth CDB on 29th of October 2010 in Nagoya recommended a moratorium on climate engineering activities. Accordingly, only scientific studies small in extent and which fulfill four criteria are granted/permitted. Most of the recent climate engineering research is allowed (e.g., that based on computer modeling), but open field experiments are prohibited.
- In preparation for its Fifth Assessment Report - planned for 2014 - the IPPC has decided to discuss the meaning of climate engineering as a possible reaction to climate change and the possible results and risks for nature and society. The IPCC arranged an expert's meeting on the subject in June, 2011 in Lima, Peru [*IPCC*, 2011].
- In a 2010 report for the U.S. House of Representatives, strategies for international coordination were discussed [*CST*, 2010]. In this context the Congressional Research Service started a study on the applicability of existing US laws and international arrangements on possible geoengineering tests as well as larger-scale implementation [*Bracmort et al.*, 2010]. In this context, the Government

Accountability Office compiled an overview on climate engineering research activities of US-federal institutions [*GAO*, 2010].

- In cooperation with the initiative of the U.S. House of Representatives, the *Science and Technology Committee* of the British parliament compiled a report for a possible international regulation of climate engineering [*STC*, 2009]. Because the technologies and procedures greatly differ between different potential strategies for geoengineering, they concluded that regulation measures would need to be explicitly adapted to the specific character of each approach.
- Non-governmental organizations are mostly critical about the idea of climate engineering, because they argue that it manifests the conditions which led to the climate crises in the first place. For instance, the *Action Group on Erosion, Technology and Concentration* [*ETC*, 2011] pursues a public anti-GE campaign against "geopiracy”.
- On the 29th September 2011, the European parliament considered but dismissed a resolution in which GE measures on a large scale would be opposed [*EU*, 2011].

Set within the context of this emerging regulatory debate, the various scientific-technical, economic, legal and political aspects of climate engineering are increasingly the focus of academic attention [c.f. the overview in *Kintisch*, 2010]. Following the Royal Society report [*UK-Royal-Society*, 2009], related issues and questions were discussed in a number of workshops, conferences and studies:

- In 2009, the *International Risk Governance Council* (IRGC) and other organizations conducted a workshop in Lisbon. The resulting working paper supports research on climate engineering and outlines a framework for international regulation, including the definition “of permissible ranges/permitted areas“ of research [*Morgan and Ricke*, 2009].
- In the context of a report by the *British House of Commons*, the “Oxford Principles” were formulated, to address research regulations on climate engineering [*Rayner et al.*, 2009]. The five principles suggest: (i) regulating geoengineering as a public good, (ii) letting the public take part in the decision-making process, (iii) disclosing the results of research, (iv) having an independent

impact assessment conducted, and (v) only beginning with any implementation after a governance process is completed.

- Corresponding proposals and recommendations were also made at the *Asilomar Conference* in 2010, which pleas for a responsible handling of climate engineering. Voluntary guidelines were discussed, which include cooperative research that involves the public. An international climate engineering regulation would be based on five principles, namely that research in this field: (i) should benefit humanity and the environment, (ii) be conducted openly and cooperatively, (iii) permit an independent technical assessment, (iv) define the limits of accountability in the context of new governance and monitoring mechanisms, and (v) involve the public during the complete process.
- In the US, the “Bipartisan Policy Center“ [*BPC*, 2011] formed a task force that presented a report in October 2011 on the possible effectiveness, feasibility and the consequences of climate engineering technologies, as well as options for risk management. Leading experts from different areas are developing recommendations for the US government with regard to the research in geoengineering and supervision strategies.
- In the UK, a 2010 joint initiative of the *British Engineering and Physical Sciences Research Council* (EPSRC) and the *Natural Environment Research Council* (NERC) was launched to perform research and an impact analysis of geoengineering measures [*EPSRC/NERC*, 2010. Potential means, efficiencies and consequences of procedures for Solar Radiation Management are being examined, while maintaining the involvement of the public. NERC supports other public discourse activities about geoengineering to explore public assessments and to communicate better future research possibilities [*NERC*, 2011]. However, efforts focused on Enhanced Weathering have yet to emerge.
- Several studies and conferences in Germany in 2011 show a growing interest of scientists and politicians in the subject of climate engineering, for example the study of the *German Federal Environmental Agency* [*Umweltbundesamt*, 2011] and a scoping study by the *Kiel Earth Institute* in October 2011, focused on assessing the application and the regulation of climate engineering [*Rickels et al.*, 2011].

These various discussions provide valuable input towards formulating strategies for research and possible implementation of any geoengineering scheme. The majority of geoengineering governance discussions have focused on solar radiation management, with particular emphasis on preventing adverse environmental effects. As the effectiveness of carbon dioxide removal technologies is dependent on the practices used for deployment (material processing, transport, application), and the size of the industry is several orders of magnitude larger than SRM, the regulatory framework is likely to be substantially different. Continued efforts to understand the scope for Enhanced Weathering will need to carefully adjust to this changing regulatory and ethical environment, in order to legitimize the results from the ongoing research.

References:

BPC (2011), Task Force On Climate Remediation Research: Geoengineering: A National Strategic Plan for Research on the Potential Effectiveness, Feasibility, and Consequences of Climate Remediation Technologies. .

Bracmort, K., R. K. Lattanzio, and E. C. Barbour (2010), Geoengineering: Governance and Technology Policy, edited by C. R. Service, Washington D.C.

Crutzen, P. J. (2006), Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma?, *Climatic Change*, *77*(3-4), 211-219.

CST (2010), Engineering the climate: Research needs and strategies for international coordination, edited by C. o. S. a. Technology, U.S. House of Representatives, (Chairman Bart Gordon), Washington.

Elliott, S. M., and H. P. Hanson (2003), Discussion - Syndication of the earth system: the future of geoscience?, *Environmental Science & Policy*, *6*(5), 457-463.

EPSRC/NERC (2010), Climate Geoengineering Sandpit.

ETC (2011), Geopiracy: The Case Against Geoengineering.

EU (2011), European Parliament resolution of 29 September 2011 on developing a common EU position ahead of the United Nations Conference on Sustainable Development (Rio+20), Strasbourg, edited.

GAO (2010), Climate Change: A Coordinated Strategy Could Focus Federal Geoengineering Research and Inform Governance Efforts. Report to the Chairman, Committee on Science and Technology, House of Representatives, edited, U.S. Government Accountability Office, Washington, D.C.

Hartmann, J., J. K. Levy, and N. Okada (2006), Managing surface water contamination in Nagoya, Japan: An integrated water basin management decision framework, *Water Resources Management*, *20*(3), 411-430.

IMO (1996), London Convention and Protocol: Convention on the Prevention of the Marine Pollution by Dumping of Wastes and Other Matter 1972 and 1996 Protocol Thereto, edited by I. M. Orginazation, International Maritime Orginazation, London.

IPCC (2011), Joint IPCC Expert Meeting of WGI, WGII, and WGIII on Geoengineering, 3.

Kintisch, E. (2010), *Hack the planet. Science's best hope – or worst nightmare – for averting climate catastrophe*, 288 pp., John Wileys & Sons, New Jersey.

Kravitz, B., A. Robock, O. Boucher, H. Schmidt, K.E. Taylor, G. Stenchikov, and Michael Schulz (2011), The Geoengineering Model Intercomparison Project (GeoMIP), Atmos. Sci. Let. 12: 162–167

Levy, J. K., J. Hartmann, K. W. Li, Y. B. An, and A. Asgary (2007), Multi-criteria decision support systems for flood hazard mitigation and emergency response in urban watersheds, *Journal of the American Water Resources Association*, *43*(2), 346-358.

Morgan, G. M., and K. Ricke (2009), Cooling the Earth through solar radiation management: The need for research and an approach to its governance.

NERC (2011), Experiment Earth? Report on a public dialogue on geoengineering, 89.

Parkhill, K., and N. Pidgeon (2011), Public Engagement on Geoengineering Research, Preliminary Report on the SPICE Deliberative Workshops. Understanding Risk Working (2011-11), 29.

Plate, E. J. (2002), Flood risk and flood management, *Journal of Hydrology*, *267*(1-2), 2-11.

Proelss, A., and K. Güssow (2011), Climate Engineering - Instrumente und Institutionen des internationalen Rechts*Rep.*, 99 pp, Kiel.

Rayner, S., R. C., J. Savulescu, N. Pidgeon, and T. Kruger (2009), Memorandum on draft principles for the conduct of geoengineering research.

Rickels, W., et al. (2011), *Gezielte Eingriffe in das Klima? Eine Bestandsaufnahme der Debatte zu Climate Engineering. Sondierungsstudie für das Bundesministerium für Bildung und Forschung.*

Scheffran, J. (2006), Tools in Stakeholder Assessment and Interaction, in *Stakeholder dialogues in natural resources management and integrated assessments: Theory* and practice, edited by S. Stoll-Kleemann and S. Welp., Springer, Berlin.

Schmidt, H., K. Alterskjær, D. Bou Karam, O. Boucher, A. Jones, J. E. Kristjansson, U. Niemeier, M. Schulz, A. Aaheim, F. Benduhn, M. Lawrence, and C. Timmreck (2012) Solar irradiance reduction to counteract radiative forcing from a quadrupling of CO2: climate responses simulated by four earth system models, Earth Syst. Dynam., 3, 63–78.

Schneider, S. H. (2008), Geoengineering: could we or should we make it work?, *Philos T R Soc A*, *366*, 3843-3862.

Shidawara, M. (1999), Hazard map distribution, *Urban Waters*, *1*, 125-129.

STC (2009), The regulation of geoengineering. Fifth report to the House of Commons. Session 2009–10.

UK-Royal-Society (2009), *Geoengineering the climate: science, governance and uncertainty*, The Royal Society, London, UK.

Umweltbundesamt (2011), *Geo-Engineering: effective climate protection or megalomania?*,, UBA, Dessau.

van Ast, J. A., and S. P. Boot (2003), Participation in European water policy, *Physics and Chemistry of the Earth*, *28*(12-13), 555-562.

Figure captions:

Figure SI-1: A proposed concept for multi-stakeholder assessment and management of Enhanced Weathering, adapted from Scheffran (2006).