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Carbon Dioxide Efficiency of Terrestrial Enhanced Weathering

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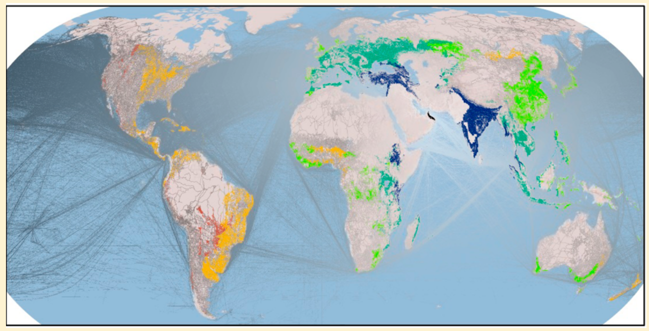
Supporting Information

ABSTRACT: Terrestrial enhanced weathering, the spreading of ultramafic silicate rock flour to enhance natural weathering rates, has been suggested as part of a strategy to reduce global atmospheric CO_2 levels. We budget potential CO_2 sequestration against associated CO_2 emissions to assess the net CO_2 removal of terrestrial enhanced weathering. We combine global spatial data sets of potential source rocks, transport networks, and application areas with associated CO_2 emissions in optimistic and pessimistic scenarios. The results show that the choice of source rocks and material comminution technique dominate the CO_2 efficiency of enhanced weathering. CO_2 emissions from transport amount to on average 0.5−3% of potentially sequestered CO_2. The emissions of material mining and application are negligible. After accounting for all emissions, 0.5−1.0 t CO_2 can be sequestered on average per tonne of rock, translating into a unit cost from 1.6 to 9.9 GJ per tonne CO_2 sequestered by enhanced weathering. However, to control or reduce atmospheric CO_2 concentrations substantially with enhanced weathering would require very large amounts of rock. Before enhanced weathering could be applied on large scales, more research is needed to assess weathering rates, potential side effects, social acceptability, and mechanisms of governance.



INTRODUCTION

Rising levels of atmospheric CO_2 may cause substantial challenges for human society. Stagnation in efforts to cut anthropogenic CO_2 emissions has led to the proposal of technological solutions for capturing and storing atmospheric CO_2.[1−5] Terrestrial enhanced weathering was suggested as one of these solutions.[6−8] The term "terrestrial enhanced weathering" is commonly used for the application of rock powder to suitable application areas to increase natural chemical weathering rates.[7−11]

Natural chemical silicate rock weathering is a major geological sink of atmospheric CO_2.[12−14] The release of cations during mineral weathering binds dissolved CO_2 to form bicarbonate and carbonate ions, which are then transported to the ocean. Annually, natural chemical silicate weathering consumes about 1 Gt of atmospheric CO_2.[15−17] Chemical weathering of forsterite is exemplary of the process (eq 1)

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg_2^{+} + 4HCO_3^{-} + H_4SiO_4 \quad (1)$$

Theoretically, based on stoichiometry and mass, the weathering of a 4 mm thick layer of forsterite (Mg-olivine) spread over the entire terrestrial land mass could consume all atmospheric CO_2.[7] In practice, there are limits to sequestration potential. Silica saturation state, for example, could limit the CO_2 sequestration in humid tropical regions to 3.7 Gt CO_2 a^{-1},[18] although forsterite saturation may substantially reduce that value.[8] Furthermore, carbonate minerals may precipitate, which would liberate up to half of the sequestered CO_2 to the atmosphere,[19] but it is unclear if the weathering rates suffice to supersaturate solutions with respect to carbonate phases. If carbonates precipitate, the remaining CO_2 will likely be fixated for millions of years.[2,12] All of the key technologies required for terrestrial enhanced weathering are mature and already used on regional scale for fertilization or pH management of agricultural and forest soils. However, the industry and associated environmental impact of up-scaling this technology require consideration. Possible side effects of terrestrial enhanced weathering on, for example, river pH and alkalinity[18] or release of metals[11,20] are related to the source rock composition as well as the deployment extent and method. In addition, the availability of suitable land may be a major limiting factor,[4] which could be amplified by infrastructure requirements of transporting large volumes of rock.

Ultramafic igneous rocks have the largest carbon sequestration potential by mass and fastest dissolution rates of silicate rocks and are thus thought to be the most applicable for terrestrial enhanced weathering.[21−24] Several studies have

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Table 1. Factors Affecting the CO_2 Budget of Terrestrial Enhanced Weathering and Their Assumed CO_2 Emissions and Sequestration[a]

theme	spatial data reference	CO_2 budget reference	condition optimistic	condition pessimistic	value optimistic	value pessimistic	unit[b]	comments
source material	30		ultramafic rocks	ultramafic rocks	736	736	10^3 km^2	
potential maximum CO_2 sequestration		10	upper limit for ultramafic rocks in Figure 1 of the reference	lower limit for ultramafic rocks in Figure 1 of the reference	1.10	0.80	t CO_2 t^{-1}	
mining		9	estimated energy need (18.8 MJ t^{-1} rock) times CO_2 emission per MJ provided by ref 10	estimated energy need (18.8 MJ t^{-1} rock) times CO_2 emission per MJ provided by ref 10	−0.007	−0.007	t CO_2 t^{-1}	
comminution		10	0.6 GJ/t energy demand (Supporting Information)	2 GJ/t energy demand (Supporting Information)	−0.07	−0.22	t CO_2 t^{-1}	
roads	31	32	lower estimate	upper estimate	−59	−109	g CO_2 km^{-1} t^{-1}	
railroads	31	32	lower estimate	upper estimate	−7	−26	g CO_2 km^{-1} t^{-1}	
trails	31	32	lower estimate	upper estimate	−59	−109	g CO_2 km^{-1} t^{-1}	values taken from class "road"
rivers	33	32	lower estimate	upper estimate	−28	−35	g CO_2 km^{-1} t^{-1}	used major world rivers
buffer: 5 km around roads, railroads, trails, and rivers	self-defined	32	lower estimate	upper estimate	−59	−109	g CO_2 km^{-1} t^{-1}	values taken from class "road"
shipping lines	34	32	lower estimate	upper estimate	−5	−20	g CO_2 km^{-1} t^{-1}	
application emissions		35	1 t per ha, 80 ha per field	3 t per ha, 1 ha per field	−0.0011	−0.004	t CO_2 t^{-1}	using a factor of 2.6 to calculate CO_2 emissions from the reported diesel volume
arable land	36,37		upper estimate of proportions on cells, outside polar or arid climates.	lower estimate of proportions on cells, outside polar or arid climates.	14.7	11.8	10^6 km^2	

[a]In the budget, negative values indicate CO_2 emissions (into the atmosphere); positive values indicate CO_2 sequestration (from the atmosphere). [b]t^{-1} refers to tonnes of rock.

already investigated their carbonation potential at elevated temperatures and under elevated pCO_2 in reactors,[25−27] which is here referred to as "mineral carbonation". For mineral carbonation, formalized life cycle studies exist.[28] The capital investment required (e.g., for creating large reactors) may limit deployment.[29] Enhanced weathering, assessed here, conceptually uses soil as a "reactor", potentially negating some of the capital expenditure for mineral carbonation. Of course, these technologies are not mutually exclusive.

As a first step to investigate the feasibility of the method at the global scale, a basic carbon budget of terrestrial enhanced weathering was performed in this study to identify key areas of uncertainty for future research. Expanding on the study of Renforth,[10] which focused on the United Kingdom, this study globally constrains the net CO_2 efficiency of terrestrial enhanced weathering by applying optimistic and pessimistic scenarios of a spatially explicit carbon budget. Rock properties, mining, comminution, transport, and application are included in the analysis.

DATA AND METHODS

Spatial data sets representing source rocks, transport pathways, and potential application areas were combined with associated CO_2 emissions (into the atmosphere) and sequestration (from the atmosphere) to develop a spatially explicit CO_2 budget of terrestrial enhanced weathering. This does not account for a potential increase in biomass or crop production due to the release of geogenic nutrients during the dissolution process.[8] The main CO_2 emissions associated with terrestrial enhanced weathering are generated by mining, comminution, transport, and spreading of the rock material. For each factor in the budget, pessimistic and optimistic scenarios were defined (Table 1). The technologically simple process of spreading rock flour on agricultural areas simplifies the CO_2 budget compared to the more complex mineral carbonation in reactors. CO_2 budgets of mineral carbonation have to account for chemical conversion, beneficial reuse, transport of used minerals, and disposal, in addition to the here assessed aspects.[28] The CO_2 budget of enhanced weathering is calculated in eq 2

$$\Delta CO_2 = \text{Potential } CO_2 \text{sequestration (based on source rock properties)} - CO_2 \text{ emissions (mining} + \text{comminution} + \text{transport} + \text{application)} \quad (2)$$

ΔCO_2 will later be referred to as "CO_2 available for sequestration", which implies that this is the amount of CO_2 that could be effectively sequestered (without giving a statement of the time that takes) after subtracting the emissions from the maximum potential sequestration. The data sets representing the individual parts of the budget are provided in Table 1 and illustrated in Figure 1. All data sets were combined

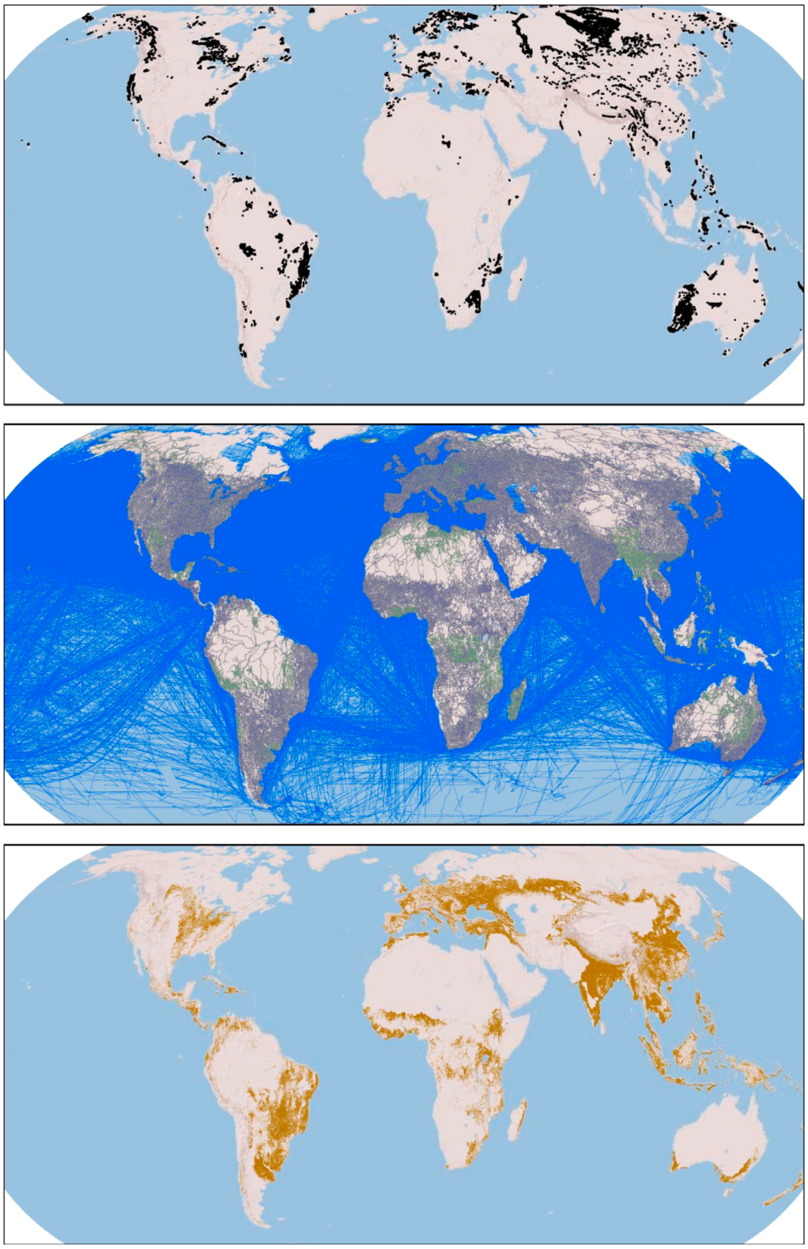

Figure 1. Spatial input data of the study. (Top) Source rock locations according to the GLiM (black, area exaggerated for visibility, coverage of potential source rocks is not exhaustive).[30] (Middle) Transport routes (colors indicate different modes of transport, but the 1 km^2 grid is too fine to be resolved in the image).[31,33,34] (Bottom) Application area.[36,37]

in a global GIS and resampled to a grid resolution of 1 km × 1 km (GIS functionalities implemented in the software ArcGIS 10 by ESRI).

Material Source Rocks. Ultramafic rocks, generally rich in the mineral forsterite, were here used as source rocks for enhanced weathering. The Global Lithological Map (GLiM)[30] contains 736,000 km^2 of rock units in which ultramafic rocks occur (Figure 1) but does not identify all ultramafic rocks globally. The source maps of the GLiM emphasize ultramafic rocks differently, and for example, in Japan, Iceland, or eastern Africa, additional ultramafic rock occurrences are likely. The maximum potential CO_2 sequestration per tonne of rock material is represented by upper (optimistic scenario) and lower (pessimistic scenario) literature values of the CO_2 sequestration of ultramafic rocks (Table 1). A source rock consisting of pure forsterite would exhibit an even higher maximum CO_2 sequestration, namely, 1.25 t CO_2 t^{-1}, based on the stoichiometry of eq 1.

Material Application Areas. Potential application areas need to (1) provide a suitable environment for chemical weathering and (2) be accessible for terrestrial material spreading. Suitable environments are moist and warm, based on the assumption that moisture is needed for dissolution reactions and temperature increases chemical weathering rates.[38] These conditions are here represented by omitting areas from "Arid climates"[37] and "Polar climates"[37] for application. Areas suitable for terrestrial spreading of rock powder were here defined by arable land cover[36] (Figure 1). Arable land seems most suitable because it is already managed, and spreading crushed rock would, notionally, require only limited new infrastructure. The land cover data provide a proportion range to which each cell is covered by arable land.[36]

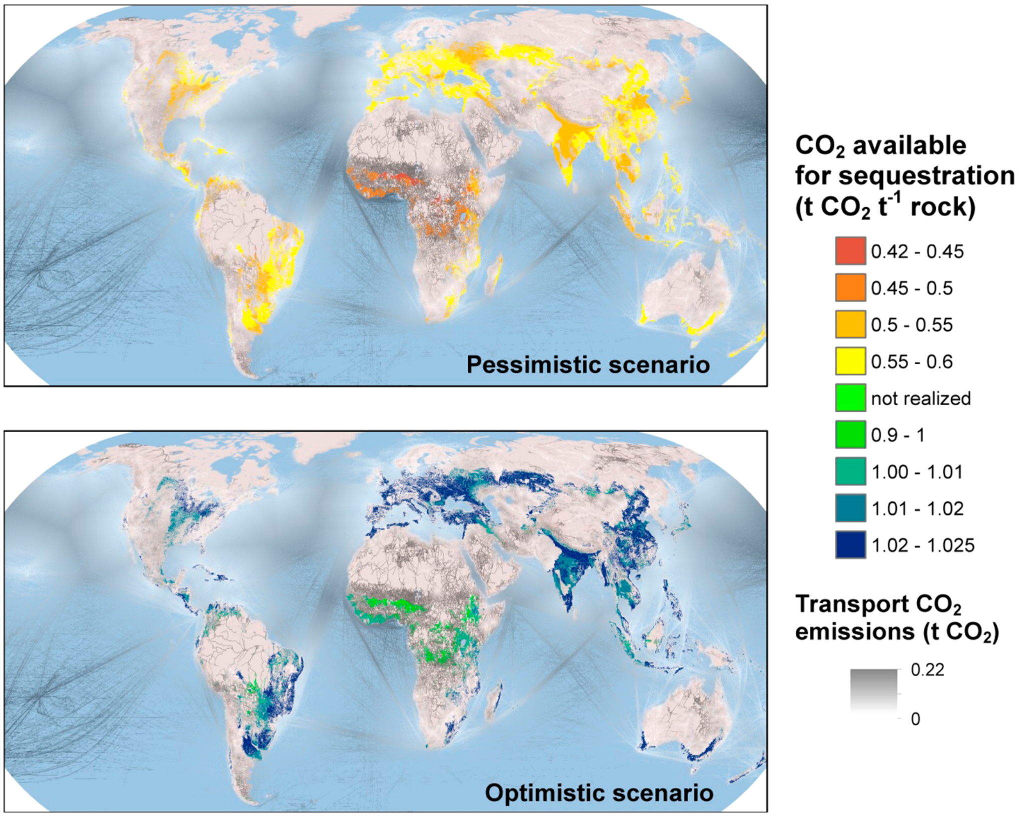

Figure 2. Available CO_2 for sequestration in the application areas. The emissions by transport are shown for comparison. The class "not realized" represents the values between 0.6 and 0.9 t CO_2 t^{-1}, which do not occur in any of the maps. Everywhere in the optimistic scenario more CO_2 is available for sequestration than anywhere in the pessimistic scenario.

The upper (optimistic) and lower (pessimistic) ends of that range are used here (Table 1). Land cover data were converted from raster into polygon data using the "Raster to Polygon" tool implemented in ArcGIS. This combines neighboring cells with the same attributes into one polygon with a unique identifier. These were reconverted into raster cells with that identifier to define individual agricultural areas and link them to the transport data sets.

Material Extraction. Extraction and application require minimal amounts of energy, which are included in the budget. The energy demand for surface extraction was reported as 18.8 MJ t^{-1},[9] which was translated into CO_2 emissions (Table 1).

Material Comminution. Size reduction of rock is achieved in a number of steps including at least one instance of crushing, followed by milling or grinding.[10] Crushing, which reduces the particle size to a diameter of about 1 mm, requires minimal energy input (5−10 MJ t^{-1} [10]). The likely necessary additional size reduction to less than 100 μm will necessitate grinding, whose energy needs are directly related to the surface area created.[9,10,25,39]

To constrain comminution energy and CO_2 emissions, we calculate the initial particle diameter required to achieve complete weathering within 1 year, given a specific weathering rate, with a shrinking core model (Supporting Information). An optimistic (pessimistic) log weathering rate[10] of −12 (−18) mol m^{-2} s^{-1} was used to calculate a grinding energy of 0.6 (2.0) GJ t^{-1}, which emits 0.07 (0.22) t CO_2 t^{-1} due to electrical energy use. As we excluded the temporal dimension from our analysis, the weathering rates remain effectively constant in the shrinking core model. The range of weathering rates between the optimistic and pessimistic scenarios is indicative of the range of values between laboratory determined kinetics of "fresh" material and heavily weathered material in catchment scale studies. Few experimental data exist that investigate silicate minerals added to the environment. As such, the treatment of kinetics for terrestrial enhanced weathering is highly uncertain.

Material Transport. Rock material for terrestrial enhanced weathering could be transported on shipping lanes (oceans, rivers), train lines, and roads. Airfreight is disregarded here because of its high associated CO_2 emissions. This study combines various global data sets to generate a routing raster from the source rock areas to the application areas. Shipping lanes are represented by a data set of known ship positions.[34] Each grid cell with at least one documented ship position in the original data is considered a potential shipping lane. For river transport, 98 major rivers of the world,[33] with an average length of 2660 km, were included and assumed to be navigable. This assumption was verified against available maps of navigable waterways. Only the upper reaches of the rivers may be unsuitable for shipping, but the resulting underestimation of transport CO_2 emissions should be small, as 1000 km transportation on rivers emits only 0.03 (0.07) t CO_2 t^{-1} less than on roads in the optimistic (pessimistic) scenario. Land transport routes were derived from the VMAP0 data set,[31] which includes global vector maps of roads, pathways, railroads, structures, and trails. The vector maps were converted to raster data sets with a 1 km × 1 km grid resolution. Some data provided different subtypes of roads, which were generalized to the classes in Table 1. All routes represented in the data sets allow material transport. The class "structure" was omitted, because it contained only few data sets. The routes represented in the VMAP0 "pathway" data set are interpreted as small roads and classed as such. To ensure connectivity within the transport network, a 5 km buffer around all mapped transport routes was assumed to be usable for transport. Areas outside the buffered transport routes were considered impassable. CO_2 emissions per kilometer vary widely between different modes of transport,[32] even for given vehicle types with varying load or driving style.[40] The CO_2 budget includes upper (pessimistic) and lower (optimistic) ends of reported provided CO_2 emission ranges per km and tonne [32] (Table 1). These values are similar to road freight transportation emissions reported by Leonardi and Baumgartner.[41]

Transport CO_2 emissions between source rocks and application areas were calculated as minimum (mean) of a cost distance raster (ESRI ArcGIS functionality) per continuous area of arable land in the optimistic (pessimistic) scenario. The calculations were performed using the "Zonal Statistics" tool implemented in ArcGIS. The optimistic scenario considers the minimum transport emissions per area, assuming that as soon as the material arrives at the application area, the application emissions cover the transport on the field (possibly an underestimation for large agricultural areas consisting of many fields). The pessimistic scenario considers the mean transport emissions per application area, which certainly overestimates the transport emissions in many cases.

RESULTS

Globally, 736,000 km^2 of suitable source rock areas are mapped. Potential application areas for terrestrial enhanced weathering amount to 14,700,000 (11,800,000) km^2 in the optimistic (and pessimistic) scenario (Figure 1). Throughout the text, results for the pessimistic scenario are presented in parentheses.

The rock flour spread on the application areas can potentially sequester up to 1.1 (0.8) t CO_2 t^{-1} (t^{-1} means "per tonne of rock") in the optimistic (and pessimistic) scenario. Before transport to the application areas, the source rocks need to be mined (extraction) and their grain size sufficiently reduced (comminution), which emits 0.074 (0.229) t CO_2 t^{-1}. Spreading the material on the application areas emits 0.001 (0.004) t CO_2 t^{-1}. The emissions associated with these three aspects are spatially static; they do not change with distance between source rocks and application areas.

Subtraction of the spatially static emissions leaves CO_2 for 17,000 (5000) km transport on road or 140,000 (21,000) km on railroad until the emissions would exceed the potential maximum CO_2 sequestration. A total of 89% of the application areas are connected to the transport network. The transportation CO_2 emissions from source to application areas average 0.007 (0.022) t CO_2 t^{-1}, which amounts to 0.7% (4.0%) of the potential CO_2 sequestration after accounting for the spatially static emissions. Even the maximum transport emissions in the optimistic scenario do not exceed the difference between the spatially static emissions of the optimistic and pessimistic scenarios. This implies that the smallest available CO_2 for sequestration at any application area in the optimistic scenario is higher than the highest available CO_2 in the pessimistic scenario (Figure 2). Transport costs are thus not a major constraint to the effectiveness of the enhanced weathering technique. Source rock occurrences unrepresented in the GLiM could shorten transport routes and further reduce the average transport emissions at global scale.

Combining all factors, the available CO_2 for sequestration (ΔCO_2: maximum potential CO_2 minus emissions, eq 2) differs strongly for both scenarios. After subtracting all emissions, on average 1.02 (0.54) t CO_2 t^{-1} are available for sequestration at the application areas in the optimistic (pessimistic) scenario. If terrestrial enhanced weathering were used to sequester 10% of the 9.1 Gt CO_2−C emitted by fossil fuel combustion and cement production in 2010,[42] 0.9 (1.7) Gt of ultramafic rock material would need to be weathered according to the optimistic (pessimistic) scenario. For comparison, the estimated present total mass movement by humans is 40−45 Gt a^{-1}.[43] Certainly, extracting, moving, and spreading these large additional masses would have strong socioeconomic and environmental consequences.

DISCUSSION

In the optimistic scenario, associated emissions reduce the available CO_2 for sequestration only slightly below the potential maximum CO_2 sequestration (Figure 3). The pessimistic scenario shows a substantial reduction of the available CO_2 for sequestration, mainly because of the assumed less favorable rock composition (and the resulting smaller maximum CO_2 sequestration) and increased CO_2 emissions of comminution (Figure 3). The effect on the difference between the optimistic and pessimistic scenarios is largest for the potential maximum CO_2 sequestration. It is responsible for 80.6% of the variability of the available CO_2 for sequestration in a Monte Carlo Simulation (100,000 draws, Oracle Crystal Ball software, assuming a uniform distribution between optimistic and pessimistic values of all parameters). The second most sensitive parameter is comminution, contributing 19.2% to the variability. Efficiency improvements and renewable energy usage could reduce the associated CO_2 emissions below the optimistic scenario assumed here. Uncertainty in comminution requirements is largely down to uncertainty in weathering rates. The slower the weathering rate for a given surface area, the more processing is required to produce the same dissolution per mass. Experimental evidence is needed that examines the dissolution kinetics in various potential application environments, considering, for example, climate, soil hydrology, and land use. Chemical weathering rate constants (per surface area of rock) have also been shown to increase with finer material as a result of "mechano−chemical activation".[25,39] However, only a small number of studies explore this in silicate minerals, and the impact on weathering rates in soils remains unclear.[9] The emissions of mining, application, and also transport (on average) are negligible for the variability of CO_2 emissions

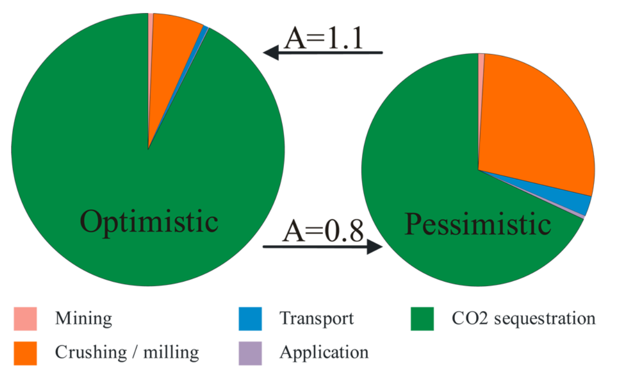

Figure 3. CO_2 budgets per tonne of rock material according to the optimistic scenario and pessimistic scenario. The area (A) of the pies represents the potential maximum CO_2 sequestration of each scenario.

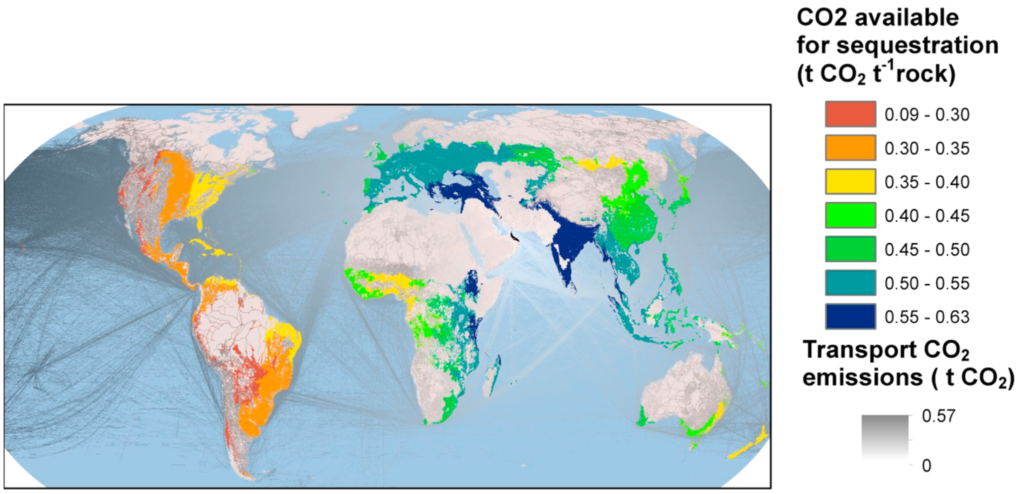

Figure 4. Conservative scenario of terrestrial enhanced weathering CO_2 sequestration efficiency using the Samail Ophiolite as source rock (marked in black on the map, located in Oman). Because the figures do not resolve the high original data resolution, visual representations of the same application areas differ between fig. 2 and fig. 4.

between the positive and negative scenarios (0%, 0%, and 0.2%, respectively). The sensitivity analysis suggests that investigations of suitable source rocks, energy requirements of comminution, and mineral reactivity in the environment are critical in assessing the potential of terrestrial enhanced weathering.

Mineral reactivity, and thus weathering rates, depend on a large number of complex environmental parameters.[8] While chemical weathering rates determined in controlled laboratory experiments (e.g., far from equilibrium and strongly influenced by temperature[44] and pH[45]) can be used as an upper estimate, the large difference of rates reported by catchment studies prevents precise assessment of terrestrial enhanced weathering with laboratory analyses. Only dedicated experiments conducted to assess dissolution kinetics in specific conditions could quantify extrinsic environmental impacts (e.g., temperature or pH) on chemical weathering rates in the field.[21,46] Pertinent to this is the influence of plants and microorganisms on chemical weathering (see Manning and Renforth[47] for discussion). A comparison of five catchments in Iceland reported a 2- to 10-fold vegetation-related increase of chemical weathering rates depending on vegetation type and mineral.[48] Similarly, a correlation between vegetation type and weathering induced bicarbonate fluxes was shown for 338 catchments in North America.[22] Field studies also highlighted the potential of microorganisms[49] and fungi[50,51] to increase weathering rates, which are ubiquitous in natural environments.[52] The biogenic increase of chemical weathering rates could allow comminution to larger grain sizes, which would save energy and improve the CO_2 budget. However, a lot more research on the controls of potential rates of enhanced weathering is needed before a qualified quantification of the temporal dimension of this technique will be feasible.

In addition, enhanced weathering was reported to improve soil and plant productivity in agriculture. One widely applied method of enhanced weathering of carbonate rocks is agricultural liming to raise pH values of acidic soils, which already significantly impacts, for example, alkalinity flux in the Ohio River Basin.[53] Enhanced weathering of silicate rocks could benefit the primary agricultural use of the application areas. The released silicon is a beneficial nutrient for many plants;[54] it enhances resistance of rice to certain diseases[55] and helps some grasses to defend against herbivores.[56] In addition, trace contents of phosphorus and other elements in the weathering rock flour could increase the productivity of some agricultural areas.[57] Alternatively, metals released by the weathering rock powder could inhibit plant growth and use.[11] These effects particularly impact the choice of source rocks to optimize the mineral content according to the needs in the application areas. The small proportion of transport emissions to the CO_2 budget suggests that the choice of source rocks should favor optimal mineral content over proximity to the application areas. The effect of enhanced weathering on agricultural output will be one of the main factors determining the success of the method. Thus, not only regarding enhanced weathering as a CO_2 removal method but also regarding alternative fertilization methods in the face of dwindling phosphate rock resources,[58] the potential effects of enhanced rock weathering on agricultural productivity[59] need more research. On the basis of these effects, enhanced weathering by spreading ultramafic rock powder may also improve the efficiency of other proposed CDR techniques, namely, biochar or afforestation.

One specific geological unit, the Samail Ophiolite in Oman, was suggested as the location for carbon management by in situ carbonation, and its carbon sequestration potential is therefore well researched.[60] To explore its potential for enhanced weathering, and as an example for the effect of transportation, we ran the transport cost routing model with the Samail Ophiolite, represented in the geological map of the Middle East,[61] as single source rock (Figure 4). Abundantly available Harzburgites from the Samail Ophiolite contain 25% Mg by weight,[62] which translates to a potential maximum CO_2 sequestration of 0.89 t CO_2 t^{-1}. After subtracting the pessimistic scenario emissions, treating the large agricultural areas in Europe and most parts Southeast Asia with material of the Samail Ophiolite would still sequester half a tonne CO_2 per tonne of rock (Figure 4). Even transport to North America would allow some CO_2 sequestration, and only in the remotest areas of the Americas is the available CO_2 for sequestration reduced below 0.3 t CO_2 t^{-1} by transport emissions (Figure 4).

Regarding the huge logistics necessary for global application, terrestrial enhanced weathering can only be one piece of the puzzle to control or reduce atmospheric CO_2 levels. This study highlights that associated emissions do not exceed the carbon sequestration potential for most application areas even under pessimistic assumptions. However, the closer the budget approaches zero, the higher the unit cost (expressed as net carbon sequestration potential, GJ tCO_2^{-1}). Combining the assumptions of energy use for extraction, comminution, and spreading (Table 1), converting the transport emissions into energy requirements (assuming an emissions intensity of 77 gCO_2 MJ^{-1} [63]), and normalizing against net carbon sequestration, the total energy requirements of terrestrial enhanced weathering is 1.6 (9.9) GJ per tonne of CO_2 sequestered via chemical weathering not accounting for the further biological biomass production possible in case of optimized biogeochemical land management. This range is similar to other technologies that propose to remove carbon dioxide from the atmosphere.[64]

Terrestrial enhanced weathering could be targeted in regions with high potential weathering rates or on soils depleted in cations and subject to biological carbon management, for example, afforestation, where suitable rocks would provide nutrients for biological carbon storage. Large uncertainties in the budget, weathering rates, and possible side effects on soil productivity highlight the need for more research before practical application of enhanced weathering might commence.

■ ASSOCIATED CONTENT

Supporting Information

Details of the used shrinking core model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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