

Passive Sequestration of Atmospheric CO₂ through Coupled Plant–Mineral Reactions in Urban soils

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ABSTRACT: Photosynthetic removal of CO₂ from the atmosphere is an important planetary carbon dioxide removal mechanism. Naturally, an amount equivalent to all atmospheric carbon passes through the coupled plant–soil system within 7 years. Plants cycle up to 40% of photosynthesized carbon through their roots, providing a flux of C at depth into the soil system. Root-exuded carboxylic acids have the potential to supply 4–5 micromoles C hr^{−1}g^{−1} fresh weight to the soil solution, and enhance silicate mineral weathering. Ultimately, the final product of these root-driven processes is CO₂, present in solution as bicarbonate. This combines with Ca liberated by corrosion associated with silicate mineral weathering to enter the soil–water system and to produce pedogenic calcium carbonate precipitates. Combining understanding of photosynthesis and plant root physiology with knowledge of mineral weathering provides an opportunity to design artificial soils or to plan land use in ways that maximize removal and sequestration of atmospheric CO₂ through artificially enhanced pedogenic carbonate precipitation. This process requires relatively low energy and infrastructure inputs. It offers a sustainable carbon dioxide removal mechanism analogous to the use of constructed wetlands for the passive remediation of contaminated waters, and is likely to achieve wide public acceptance.



INTRODUCTION

Rising atmospheric CO₂ concentrations contribute to climate change, and have done so for several thousand years, since the dawn of agriculture.¹ At present, there seems to be little prospect of rapid reduction in emissions, and a number of scenarios for future atmospheric CO₂ concentrations have been proposed.² In addition to reductions in emissions, it is important to consider mechanisms that can remove CO₂ from the atmosphere, including both carbon capture and subterranean storage, passive removal through both enhanced weathering of silicate minerals such as olivine, and the carbonation in soils of calcium silicate minerals. These approaches supplement those that focus on the role of soils in accumulating organic carbon.^{3–5}

The magnitude of the problem of mitigating rising atmospheric CO₂ concentrations is considerable.⁶ To maintain these at current levels, it is proposed that it will be necessary to identify and implement at least 7 approaches (referred to as “stabilization wedges”⁶), each capable of removing or preventing the emission of 1 Gt C annually, by 2050.

Recently, we have investigated the accumulation of carbon as calcium carbonates in urban soils.^{7,8} These are typically characterized by the presence of material derived from artificial sources, including cement-based materials used in construction and incorporated into the soil following demolition.⁷ We have found⁹ that the amount of carbon stored as calcium carbonate

(calcite) within such soils is of the order of 300 t ha^{−1}, accumulating at a rate of 25 ± 12.8 t C ha^{−1} a^{−1}. This is almost twice the quantity of C reported⁵ as typical for cultivated agricultural soils (190 t ha^{−1}), and represents (in terms of lifetime once formed) a “perpetual sink for atmospheric CO₂”.¹⁰ Use of C and O isotope ratios in early studies of pedogenic carbonate minerals^{11–13} showed that these had distinctively negative values, and could be attributed to C (and O) isotope fractionation within plants as a consequence of photosynthesis. Interpretation of C and O isotopes within pedogenic carbonates showed that in some cases all of their carbon is derived from the atmosphere via photosynthesis, and different photosynthetic pathways can be distinguished.^{13,14} More recent work demonstrated that carbon isotope studies of pedogenic carbonates could be closely related to vegetation changes over time and in response to differences in rainfall.^{14–16} Thus pedogenic carbonate minerals in natural vegetated soils owe their origin ultimately to removal of atmospheric CO₂ by photosynthesis.

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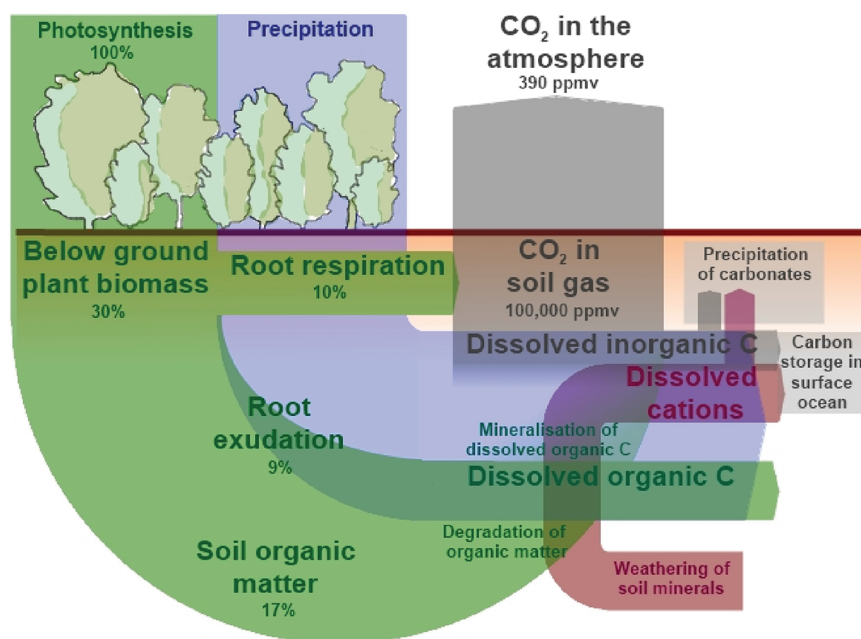
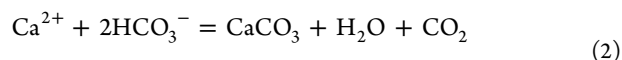
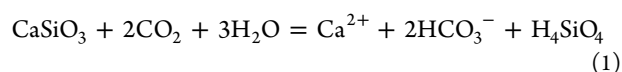


Figure 1. Simplified trajectory for the fate of root exudate carbon, showing percentages of Gross Primary Production C in specific subsurface pathways.¹⁹

Considering the possible global impact of carbonation of materials that are generated by industrial manufacturing activity (cement production, steel production and coal-fired electricity generation), we have shown that the total amount of calcium, magnesium and iron silicates produced each year has a terrestrial carbonation potential of the order of 700–1200 million tonnes CO₂.⁸ While the precipitation of carbonate in soils is an easily measurable, and in some cases a visible, sink for atmospheric CO₂, additional draw-down of CO₂ is possible if the weathering products remain dissolved, through increased solution alkalinity. For instance, the magnesium silicate mineral forsterite (Mg₂SiO₄) dissolves to form Mg²⁺ and HCO₃[−] in solution. With sufficiently rapid weathering, the solution could become supersaturated with respect to magnesium carbonate minerals (e.g., magnesite, MgCO₃), which would precipitate if kinetics permit. However, if the solution was transported (via runoff, streams and rivers) to the surface ocean, the weathering products remain dissolved, and the carbon would be stored as ocean alkalinity.¹⁷ Over long (geological) time periods this additional alkalinity would precipitate out of solution through incorporation into the shells of surface ocean microorganisms (e.g., coccolithophores). But on short (human) time scales, small increases in alkalinity are thought to be relatively stable.¹⁸ Approximately 1.7 moles of carbon dioxide can be captured for every mole of cation.¹⁷ Thus enhanced weathering (i.e., taking additional alkalinity into account; eq 1) of waste materials has a maximum carbon capture potential of 1190–2040 million tonnes of CO₂.

It is important to recognize that when artificial “wastes” are involved in carbonation reactions, often they are derived from materials manufactured by calcining limestones, and their weathering in soils merely replaces C that was lost during the manufacturing process. General reactions for the weathering of a calcium silicate mineral and the formation of mineral carbonates and alkalinity are given in eqs 1 and 2:



Because of the additional alkalinity, enhanced weathering extends beyond simple recovery of CO₂ lost through calcining during manufacture. Combined, mineral weathering and carbonate production (eq 1,2) are equivalent to 30–50% of one of seven mitigation targets (“stabilization wedges”) proposed by Pacala and Socolow.⁶ The potential carbon capture value of carbonation of mineral wastes is expected to increase, given that their production is likely to increase over the coming century. This is in addition to the carbonation of naturally occurring calcium silicate minerals, as a consequence of rock weathering.

Urban soils commonly contain calcium silicates and other construction/demolition-derived calcium minerals (such as gypsum, CaSO₄·2H₂O, and portlandite, Ca(OH)₂). Recognition that such soils have the potential to capture carbon, and are locations in which enhanced weathering can be included in their design, leads to the concept of “carbon capture gardens” or landscaping that exploits the interaction between growing plants and minerals in the subsurface. This concept is attractive to a number of stakeholders; it is easily explained to nonexperts and provides developers with an opportunity to make use of materials that arise from demolition by virtue of their inherent carbon capture function.

Carbonate mineral precipitation is controlled by the saturation state of the soil solution, and that depends on the activities of dissolved species (divalent cations and carbonate). In arid environments, evaporation encourages saturation with respect to specific minerals, which then precipitate. In humid environments, saturation can be achieved through other processes which increase the activities of dissolved species. For carbonate minerals to reach saturation and precipitate in engineered soils, it is important to assess the extent to which it

Table 1. Examples of Carboxylic Acid Contents of Soil Solutions,²³ Giving Total Molarity of C and Estimated H⁺

	formate (CHO ₂ ⁻)	acetate (C ₂ H ₃ O ₂ ⁻)	oxalate (C ₂ O ₄ ²⁻)	malate (C ₄ H ₄ O ₅ ²⁻)	citrate (C ₆ H ₅ O ₇ ³⁻)	total C	H ⁺
	Micromolarity						
moles of carbon per moles of anion	1	2	2	4	6		
<i>Lupinus albus</i> root mat					4700	28 200	7050
ultic hapludalf cultivated soil		2737				5474	1369
typic hapludalf cultivated soil	579	786			122	2883	866
<i>Trifolium</i> rhizosphere soil		1430		1472		8748	2187
<i>Elytrigia</i> rhizosphere soil	563	630	198			2219	795
soil containing <i>Elytrigia</i> residues	2277	3151	417			9413	3131
<i>Picea albes</i> podzolic topsoil	177	1829		165	370	6715	1723

Table 2. Rates of Production of Malate and Citrate from Plant Roots,²³ with Equivalent Carbon and Proton (H⁺) Production Rates

	picomol g _{FW} ⁻¹ s ⁻¹						
	malate	citrate	nanomoles C g _{FW} ⁻¹ s ⁻¹	micromoles C g _{FW} ⁻¹ hr ⁻¹	nanomoles H ⁺ g _{FW} ⁻¹ s ⁻¹	micromoles H ⁺ g _{FW} ⁻¹ hr ⁻¹	
number of carbons	4	6					
lupin (proteoid roots)	141	158	1.5	5.4	0.4	1.4	
maize (whole root)	165	38	0.9	3.2	0.2	0.8	
wheat (root tip)	338	3.1	1.4	4.9	0.3	1.2	
mean			1.3	4.5	0.3	1.1	

is the availability of mineralized C, present in solution as a carbonate species and ultimately derived from plants and hence from photosynthesis, or whether it is the availability of Ca or Mg, derived from mineral dissolution during weathering, that limits carbonate precipitation.

In this paper, we explore limiting factors, in terms of reagent availability, that govern coupled plant–soil systems designed to optimize carbon capture in engineered soils, within the framework of an innovative conceptual model. We synthesize information from different published sources, drawing from disparate disciplines, to provide a consistent set of data that allows us to assess the feasibility of the process. Our first objective is to assess available information from laboratory experiments concerning the formation and chemical composition of plant root exudates. Second, we consider the occurrence and origin of bicarbonate in surface waters at a catchment scale. Third, we use published laboratory dissolution rate data to assess the availability of cations, focusing on Ca (given its preponderance over Mg in the majority of bulk artificial silicate products). Importantly, we demonstrate that despite inconsistencies in reporting and units, the rate-limiting step from field studies appears to be the availability of Ca, not that of C.

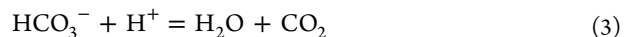
MATERIALS AND METHODS

A conceptual model was developed for CO₂ capture and storage that considers the availability of Ca and dissolved carbonate through the weathering of soil minerals, leading to pedogenic carbonate precipitation. The composition of plant root exudates was taken from published reports of laboratory experiments, and has been recalculated, using consistent units, to give the equivalent inorganic carbon product for reactions leading to complete mineralization. For comparison, the amount of inorganic C leaving catchments via drainage has been obtained from published sources. The availability of divalent cations, in particular Ca²⁺, was assessed using independently collated laboratory dissolution rate data for calcium-bearing minerals that occur within artificial cement and related products. The amount of inorganic C derived from plant root exudate formation and the availability of Ca from

mineral dissolution were compared, to assess the feasibility of the conceptual model and to identify practical considerations for its application.

RESULTS AND DISCUSSION

Conceptual Model. Figure 1 shows the conceptual model for the formation of pedogenic carbonates. Photosynthesis fixes carbon derived from the atmosphere in plant biomass, around 30% of which is below ground.¹⁹ Living root tissue produces root exudates,^{20,21} whose composition^{22–24} includes sugars (50–70% of total exudate), carboxylic acids (20–30%), and amino acids (10–20%), which provide a soluble substrate for microbial activity. Inputs from the soil surface include dead plant tissue, such as leaves and stalks, and these decompose within the soil through the action of invertebrates and microbes; this input is supplemented by material derived from death of plant roots. Irrespective of the decomposition pathway, the ultimate fate of photosynthetic carbon that enters an oxidizing soil system is to mineralize all organic carbon,²⁵ producing CO₂ in the soil gas phase, or bicarbonate species within the soil solution, in accordance with eq 3, in which bicarbonate is the dominant inorganic species between pH 6 and 10.5.²⁶



Production of Plant Root Exudates. Exudate production is known to vary from one plant species to another, and also in response to stress such as phosphate deficiency.^{20,23} While many reports describe crop plants, fewer address root exudate production in natural systems such as woodlands.^{27,28} In addition, different studies report root exudate formation using different frames of reference, meaning that direct comparison between different published sources depends on informed assumptions.

Table 1 summarizes the production of carboxylic acids for selected plant species.²³ These data show that in most cases acetate and formate are the most abundant carboxylic acids. The high citrate content reported for root mats associated with *Lupinus albus* is from a study that only determined citrate.

In Table 1, the concentrations of individual acid anions in the soil solution are expressed as micromolarity. However, the chemical formula and so the carbon content of each acid anion varies. The total micromolarity of organic C that is present in the soil solution in these acid anions has been calculated. Total C varies from 2.2 to 28 mM, representing the carbon content that is available for mineralization, and is equivalent to the maximum total inorganic carbon molarity in solution that would be produced by the complete decomposition of these carboxylic acids. Additionally, the exudation of an anion needs to be accompanied by cations to balance charge. Assuming that they comprise 50% of exuded cations,²⁰ Table 1 also shows the equivalent proton yields.

Table 1 represents a snapshot view of a soil solution at a given point in time. Information is also available concerning the rate of production of carboxylic acids from plant roots, including malate and citrate (Table 2²¹). Expressed as picomoles per gram of fresh weight root tissue (g_{FW}) per second, there is considerable variation between malate and citrate. However, when converted to the equivalent carbon flux, the total amount of exuded C varies from 0.9 to 1.5 nanomoles $g_{FW}^{-1} s^{-1}$, and this scales to 3.2–5.4 micromoles C g_{FW}^{-1} per hour or 28–48 mmol C g_{FW}^{-1} per year. This is an enormous amount of carbon, equivalent to up to approximately 0.5 g of carbon per gram of root annually. Similarly, H^+ production is of the order of 1.1 micromoles per hour for each gram fresh weight of root. It is important to note that only a small proportion of a root system is active in exudate production (e.g., root tips and root hairs). Also, root exudate production is greatest when a plant is stressed, for example through nutrient deficiency²⁹ or exposure to cations such as Al^{3+} .³⁰

Plant-Derived Carbon at a Catchment Scale. The rates of production of root exudates have been determined predominantly under laboratory or small-scale field conditions. Bicarbonate is routinely measured in analyses of natural waters, originating through a number of processes. At a large catchment scale (5×10^5 km²), it has been demonstrated that there is a major component of plant-derived carbon in dissolved bicarbonate in rivers draining basaltic rocks in India.²⁹ Although absolute concentrations of dissolved organic carbon are reported, together with C isotope data, it is not possible to estimate fluxes of C through the coupled plant–soil–bedrock system in this case.

The production of carbon by plant growth on a catchment scale can be estimated from the carbon contents in solution for waters passing through areas of wooded land in Iceland.¹⁰ This study was expressly designed to address rates of mineral weathering as a consequence of plant growth at a location where the soil is a volcanic rock free from geological carbon sources, extending earlier work and comparing vegetated vs. unvegetated land.³² Key data relating to the amount of bicarbonate in water draining from the soils that support tree growth are presented in Table 3.

The fluxes reported from Iceland¹⁰ represent an estimate of the amount of carbon that passes through a growing woodland system (both biotic and abiotic) to enter the soil solution, a proportion of which leaves as a flux to surface waters. This can be regarded as the net effect of the sequence of events shown in Figure 1. By comparison with control plots, it is demonstrated that plant growth is responsible for enhanced bicarbonate concentrations in surface waters, but there are no stable isotope data available that demonstrate this, in contrast to studies

Table 3. Bicarbonate Reported for Surface Waters Draining Forest Plots Growing on Basalt-Derived Soils in Iceland¹⁰

	pH	HCO_3^- micromoles L^{-1}	area ha	flow rate $L s^{-1}$	annual flux HCO_3^- moles ha^{-1}
bare, soil	6.78	113	121	11.8	353
bare, no soil	7.03	188	24	1.5	362
birch (southern plot)	7.21	218	594	34	911
birch (northern plot)	7.23	322	186	20.1	985
conifer	7.19	291	283	26.5	999
Gíslason et al ³⁰	7.4	477	355 000	189 100	8000

elsewhere.³¹ Similar fluxes have been reported for soil solution from the Duke Forest Free Air CO_2 Enrichment Experiment.³³

As a very first approximation, the rates of production of carbon in exudates can be extrapolated to the catchment scale on the basis of an assumed mass of roots per hectare. Root masses for loblolly pine are reported³⁴ to be 2–44 Mg ha^{-1} (dry weight), approximately equivalent to 10–200 Mg ha^{-1} FW. If all this root tissue produced root exudates at the rate of 4.5 micromoles C $g_{FW}^{-1} hr^{-1}$ (Table 2), the equivalent maximum flux would be of the order of 900 mols C per hectare, or 10 kg of carbon per hectare hourly. Similarly, root masses of 10 Mg ha^{-1} dry weight have been reported³⁵ for prairie grasslands, giving an equivalent hourly flux of 225 mols C ha^{-1} , or 2.5 kg of carbon ha^{-1} . These values are well in excess of the fluxes of bicarbonate reported in Iceland,¹⁰ which are of the order of 1 g C per hectare hourly.

Weathering of Ca and Mg Silicates in Soils. The partial pressure of CO_2 in the soil varies between 2 and 10 kPa,³⁶ which is equivalent to typical concentrations in flue gas from fossil fuel power stations. At this concentration, the pH of a pure soil solution in equilibrium with the soil gas may be as low as 4.5. Furthermore, biogeochemical activity in soils, particularly the plant and microbe exudation of organic molecules, enhances chemical weathering. The combined effects of soil solution fluxes, macrofauna (e.g., earthworm) turnover, and anthropogenic activity contribute substantially to mineral weathering.

Artificially, calcium silicate minerals enter soils through a number of routes. In urban soils, a history of demolition, especially of concrete buildings, introduces calcium silicate minerals through the incorporation of dusts and fine-grained concrete and mortar particles, as well as coarser materials (although wherever possible these are reused as a secondary aggregate). The calcium hydroxide mineral portlandite ($Ca(OH)_2$) also occurs, derived from mortars as well as cement-based materials, and gypsum ($CaSO_4 \cdot 2H_2O$) is derived from plaster products; both of these minerals dissolve rapidly compared to silicate minerals (Table 4^{37,38}). Natural Ca and Mg silicates enter soils through inclusion of quarried aggregates such as basic igneous rocks (e.g., dolerite, basalt, etc.), also in a range of particle size fractions. Natural Ca and Mg silicates also contribute to pedogenic carbonate formation; in this paper, the emphasis on artificial calcium silicates arises because they may be inherently more reactive (very fine grained, often amorphous materials), and because of the need to manage their production and eventual disposal.

Table 4. Rates of Reaction at 25°C for the Dissolution of Selected Mg and Ca Silicates and Nonsilicate Minerals for Acid and Neutral pH Reaction Mechanisms,^{37,38} and Free Energies of Reaction for Weathering of Silicate Minerals^{8a}

mineral	formula	log k moles m ⁻² s ⁻¹ acid	log k moles m ⁻² s ⁻¹ neutral	E acid/ neutral kJ mol ⁻¹	weathering rate @ pH 5, 25 °C moles m ⁻² s ⁻¹	ΔG _r kJ mol ⁻¹	ΔG _r kJ mol ⁻¹ carbonate product	log mmoles Ca g ⁻¹ hr ⁻¹
enstatite	MgSiO ₃	-9.02	-12.72	80.0/80.0	-12.70	0.14	0.14	-7.14
forsterite	Mg ₂ SiO ₄	-6.85	-10.64	67.2/94.4	-10.61	-66.8	-33.4	-5.06
anorthite	CaAl ₂ Si ₂ O ₈	-3.50	-9.12	16.6/17.8	-8.41	-57.8	-57.8	-2.85
wollastonite	CaSiO ₃	-5.37	-8.88	54.7/54.7	-8.87	-27.0	-27.0	-3.31
diopside	CaMgSi ₂ O ₆	-6.36	-11.11	96.1/40.6	-10.92	-26.2	-13.10	-5.36
tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	-8.40	-10.60	18.9/94.4	-10.60	-33.1	-4.73	-5.04
brucite	Mg(OH) ₂	-4.73	-8.24	59.0/42.0	-8.23			-2.67
portlandite	Ca(OH) ₂	-	-5.14					0.42
gypsum	CaSO ₄ ·2H ₂ O	-	-2.79					2.77
calcite	CaCO ₃	-0.30	-5.81	14.4/23.5	-5.18			0.37

^aRates of release of Ca are calculated assuming a conservative surface area of 0.1 m²/g.

Evidence from catchment studies of weathering³⁹ yields mineral dissolution rates that vary considerably (by several orders of magnitude) in the same catchment over time, or between catchments. Given this complexity, comparison between catchment and laboratory scale mineral weathering is challenging. Catchment studies so far fail to address dissolution rates for artificial minerals found in urban soils. We use laboratory-derived dissolution rates to permit a consistent assessment of the potential of enhanced weathering (Table 4).³⁷

The release of calcium or magnesium from silicate minerals depends on the reaction rate, temperature, and the surface area:volume ratio of mineral grains. Table 4 summarizes the modeled availability of Ca through dissolution of anorthite (a plagioclase feldspar), wollastonite (a calcium silicate that can be regarded as a proxy for many artificial poorly crystalline minerals that occur within Portland cement), diopside (a pyroxene) and tremolite (an amphibole). It also includes data for the nonsilicates gypsum and portlandite. For the silicate minerals, dissolution rates are given for reactions that involve protons, in accordance with known dissolution mechanisms³⁷ and the need to consider organic acids within the soil solution. Neutral rate data are used for portlandite, calcite, and gypsum, as (in contrast to the silicate minerals) these dissolve congruently into an aqueous solution.

Table 4 shows that the rates of dissolution of anorthite and wollastonite from sand-sized grains are greater than those of diopside and tremolite, although these are also inherently unstable (ΔG_r for a weathering reaction is negative) in soil systems.⁴⁰ The orders of magnitude of the availability of Ca from anorthite and wollastonite are similar to those predicted for gypsum and portlandite respectively. The pure plagioclase end member anorthite is rare compared with other plagioclase species, occurring mainly in ultrabasic igneous rocks, which are uncommon at the Earth's surface. Bytownite and labradorite plagioclase compositions are typical of basaltic igneous rocks, which are widespread in their occurrence. Plagioclase species that have less Ca than anorthite have lower dissolution rates (Figure 2), and so it is reasonable to assume that the rate of release of Ca from the most widely distributed calcium silicate minerals will be similar to, or less than, that from wollastonite (Figure 2), and of the order of 0.01 mols Ca g⁻¹ hr⁻¹ for sand-sized grains. If we assume a plant root exudate production rate of 5 micromoles C g_{FW}⁻¹ hr⁻¹ (Table 2), it is clear that the entire yield of Ca from 1 g dissolving silicate mineral would

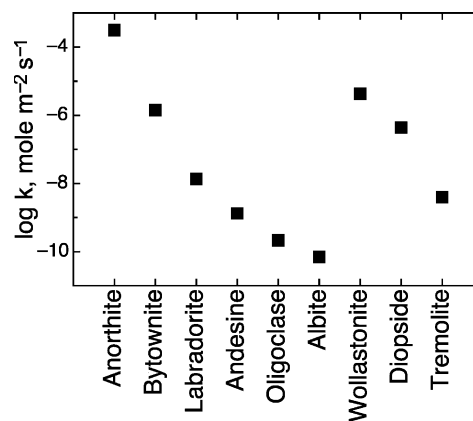


Figure 2. Variation in dissolution rate for different mineral species,³⁷ showing the systematic decrease in rate for plagioclase as it becomes less Ca-rich (anorthite is CaAl₂Si₂O₈; albite is NaAlSi₃O₈; bytownite, labradorite, andesine, and oligoclase are intermediate members of a continuous solid solution).

react to produce CaCO₃ with the exudate produced by 0.1 g of exuding plant root. Silicate mineral dissolution is likely to be limiting to carbonate formation in soil.

Table 4 also gives the dissolution rate for calcite, assuming a neutral dissolution mechanism, and it is similar in order of magnitude to diopside. Clearly, if calcite dissolves through an acid dissolution mechanism it would be rapidly (by a factor of 10⁵) removed from a soil. However, the observed persistence of pedogenic carbonates, over periods of geological time, suggest that, once formed, calcite dissolution in soils is not likely to be significant,^{14–16} probably because with limited drainage the soil solution remains saturated with respect to calcite. In soils with substantial through drainage, for example those investigated in Iceland,¹⁰ calcite saturation indices in the soil solution will be negative, and any calcite that is present in detrital grains or formed by precipitation will be removed.

Comparison with Observation. In an urban soil from a city center site in Newcastle,⁹ calcium carbonate (calcite) is reported to accumulate to a depth of 3 m at a rate of 25 ± 12.8 t C ha⁻¹ a⁻¹, which is equivalent to 2.8 kg C ha⁻¹ hour⁻¹, or 230 mols C ha⁻¹ hour⁻¹. The feasibility of calcite accumulation as a consequence of reaction between plant root exudates and Ca liberated by the dissolution of silicate minerals is now considered.

We have no information concerning the amount of plant roots within the Newcastle soil that was investigated,⁹ apart from observation of their occurrence to depths of up to 1 m, in ground dominated by cobble-sized fragments of concrete, bricks and masonry (see visual abstract). However, an accumulation rate of 230 mols C ha⁻¹ hour⁻¹ is equivalent to 23 mmol C m⁻² hour⁻¹. Assuming a rate of production of 45 $\mu\text{M C g}_{\text{FW}}^{-1} \text{ hr}^{-1}$, this requires 5 kg_{FW} m⁻² of exuding roots, or 50 Mg_{FW} ha⁻¹. This is consistent with estimates of plant root density, and although a small proportion of a root system is active in exudate production it seems reasonable that it is not the availability of plant-derived C that will limit the accumulation of calcium carbonate in such soils.

The inorganic carbon fluxes observed in vegetated plots in Iceland¹⁰ are approximately 1000 mols C ha⁻¹ a⁻¹. If fully converted to calcium carbonate, this corresponds to 1000 mols of CaCO₃, or 100 kg CaCO₃ annually. This is insufficient to account for the observed rate of accumulation in urban soils, by a factor of 250. If the flux determined by Gislason et al.³² is used, the corresponding amount of CaCO₃ that could be formed is 800 kg, a factor of 30 times lower than that observed. Both studies report solution compositions that are undersaturated with respect to calcite.

If we assume that the urban soil described above⁹ contains sand-sized calcium silicates with a dissolution rate that yields 0.01 mmol Ca g⁻¹ hr⁻¹, the amount of these in one hectare of land that is required to supply calcium at the observed carbonate accumulation rate (230 mols ha⁻¹ hour⁻¹) is 23 tonnes. This is much less than what is observed (typically equivalent to at least 10⁴ t ha⁻¹), and so in practice is unlikely to be a limiting factor, until the mineral carbonation potential is exhausted.

Implications. Soils have a major role to play in mitigation designed to remove CO₂ from the atmosphere. Importantly, human exploitation of soils has taken place for at least 10 000 years, providing a widely held wealth of experience that enables appropriate soil management practices to be adopted with confidence.

There are three ways in which soils sequester atmospheric CO₂. First, organic carbon accumulates in soils through plant growth.³ This gives a fragile carbon stock, which degrades at rates that depend in detail on the environment of accumulation. Second, lying at the interface between the geosphere and the atmosphere, soils are the location of rock weathering, which promotes dissolved inorganic carbon in the soil solution. Third, soils are host to precipitates of pedogenic carbonate minerals, representing a fixed carbon sink,¹⁰ whose stability depends on subsequent carbonate dissolution. The two processes that involve formation of carbonate or bicarbonate in solution represent perpetual¹⁰ carbon sinks; CO₂ will only return to the atmosphere if the soil solution re-equilibrates with the atmosphere, or if solution pH is reduced to low values, which in turn depend on the total solution composition.

There are two approaches that can exploit plant-driven carbonation of the coupled soil–water system. First, the evidence obtained from studies of vegetated land, where the subsoil is a basaltic igneous rock^{10,31,32} demonstrates that enhanced concentrations of dissolved inorganic carbon and occurrence of pedogenic soil carbonate minerals⁴¹ are associated with plant growth on basaltic rocks. Importantly, the depth at which pedogenic carbonates occur in soils increases with increasing rainfall.⁴² In reforestation or forest management designed to enhance carbon stocks, emphasis

should be placed on prioritizing forest growth on soils that overly or drain into basaltic igneous rocks. Such soils occur across large areas (e.g., outcrop areas for the Deccan Traps,³¹ India, and the Columbia River Basalts,⁴³ U.S., are 500 000 km² and 220 000 km², respectively). There are 14 basaltic large igneous provinces of this type globally,⁴⁴ with a widespread distribution. However, to make an appreciable contribution to CO₂ draw-down, natural fluxes will have to be increased by an order to several orders of magnitude. It is probably unlikely that this can be achieved without extraction and processing of geological materials, which has an associated carbon cost.

The second approach involves management of land that has had a history of development or industrial activity, for example “brownfield” land. Soils in these areas are highly variable in their composition, quality, and suitability for future use. In urban areas materials derived from cement manufacture commonly occur within the soil, and include concrete and mortar. As well as construction, redevelopment involves design of the landscape increasingly with the intention of including a range of ecosystem services.⁷ Carbon capture is one such service, albeit unseen and underground. It has been shown⁸ that the amounts of material arising as a consequence of industrial activity globally is substantial, with a carbonation potential of 700–1200 million tonnes of CO₂ annually, or an enhanced weathering potential of 1190–2040 million tonnes of CO₂. At present, much of this material is treated as waste, which means that regulatory requirements govern its management. There is potential for such materials to realize value as carbon sinks in soils, if appropriately managed.

In the treatment of contaminated waters, constructed wetlands (reed beds) can be used as a passive remediation process.⁴⁵ These rely on natural processes to remove dissolved contaminants, and also to remove suspended solids. They have very low energy inputs and relatively low maintenance costs compared with industrial plant and equipment, and are suitable for treating chronic and geographically isolated pollution sources. Their creation typically involves substantial community engagement. The use of soils as a way of removing atmospheric CO₂ is analogous to the use of constructed wetlands to clean up contaminated waters. The coupled plant–soil system naturally removes CO₂ from the atmosphere, and in so doing carbon is transferred to the soil. Careful design of “carbon capture gardens” and related activities provides a route to widespread, community-focused, climate mitigation.

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Notes

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REFERENCES

- (1) Ruddiman, W. F.; Kutzbach, J. E.; Vavrus, S. J. Can natural or anthropogenic explanations of late-Holocene CO₂ and CH₄ increases be falsified? *Holocene* **2011**, *21*, 865–879.
- (2) Royal Society. *Geoengineering the Climate: Science, Governance and Uncertainty*; Royal Society: London, 2009.
- (3) Lal, R. Global potential of soil carbon sequestration to mitigate the greenhouse effect. *Crit. Rev. Plant Sci.* **2003**, *22*, 151–184.
- (4) Paustian, K.; Andren, O.; Janzen, H. H.; Lal, R.; Smith, P.; Tian, G.; Tiessen, H.; Van Noordwijk, M.; Woomer, P. L. Agricultural soils as a sink to mitigate CO₂ emissions. *Soil Use Manage.* **1997**, *13*, 230–244.
- (5) Smith, P.; Milne, R.; Powlson, D. S.; Smith, J. U.; Falloon, P.; Cameron, K. Revised estimates of the carbon mitigation potential of UK agricultural land. *Soil Use Manage.* **2005**, *16*, 193–195.
- (6) Pacala, S.; Socolow, R. Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. *Science* **2004**, *305*, 969–972.
- (7) Renforth, P.; Edmondson, J.; Leake, J. R.; Gaston, K. J.; Manning, D. A. C. Designing a carbon capture function into urban soils. *Proc. Inst. Civ. Eng.: Urban Design Plann.* **2011**, *164* (2), 121–128.
- (8) Renforth, P.; Washbourne, C.-L.; Taylder, J.; Manning, D. A. C. Silicate production and availability for mineral carbonation. *Environ. Sci. Technol.* **2011**, *45* (6), 2035–2041.
- (9) Renforth, P.; Manning, D. A. C.; Lopez-Capel, E. Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide. *Appl. Geochem.* **2009**, *24*, 1757–1764.
- (10) Moulton, K. L.; West, J.; Berner, R. A. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *Am. J. Sci.* **2000**, *300*, 539–570.
- (11) Salomons, W.; Mook, W. G. Isotope geochemistry of carbonate dissolution and reprecipitation in soils. *Soil Sci.* **1976**, *122*, 15–24.
- (12) Salomons, W.; Goudie, A.; Mook, W. G. Isotope composition of calcareous deposits from Europe, Africa and India. *Earth Surf. Processes* **1978**, *3*, 43–57.
- (13) Cerling, T. E. The stable isotope composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.* **1984**, *71*, 221–240.
- (14) Landi, A.; Mermut, A. R.; Anderson, D. W. Origin and rate of pedogenic carbonate accumulation in Saskatchewan soils, Canada. *Geoderma* **2003**, *117*, 143–156.
- (15) Stevenson, B. A.; Kelly, E. F.; McDonald, E. V.; Busacca, A. J. The stable carbon isotope composition of soil organic carbon and pedogenic carbonates along a bioclimatic gradient in the Palouse region, Washington State, USA. *Geoderma* **2005**, *124*, 37–47.
- (16) Wang, D.; Anderson, D. W. Stable carbon isotopes of carbonate pendants from Chernozemic soils of Saskatchewan, Canada. *Geoderma* **1998**, *84*, 309–322.
- (17) Kheshgi, H. S. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy* **1995**, *20* (9), 915–922.
- (18) Morse, J. W.; Wang, Q.; Tsio, M. Y. Influences of temperature and Mg:Ca ratio on CaCO₃ precipitates from seawater. *Geology* **1997**, *25*, 85–87.
- (19) Kuzyakov, Y.; Domanski, G. Carbon input by plants into the soil – review. *J. Plant Nutr. Soil Sci.* **2000**, *163*, 421–431.
- (20) Ryan, P. R.; Delhaize, E.; Jones, D. L. Function and mechanism of organic anion exudation from plant roots. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **2001**, *52*, 527–560.
- (21) Kuzyakov, Y.; Hill, P. W.; Jones, D. L. Root exudate components change litter decomposition in a simulated rhizosphere depending on temperature. *Plant Soil* **2007**, *290*, 293–305.
- (22) Krafczyk, I.; Trollenier, G.; Beringer, H. Soluble root exudates of maize: Influence of potassium supply and rhizosphere micro-organisms. *Soil Biol. Biochem.* **1984**, *16*, 315–322.
- (23) Jones, D. L. Organic acids in the rhizosphere – a critical review. *Plant Soil* **1998**, *205*, 25–44.
- (24) Hütsch, B. W.; Augustin, J.; Merbach, W. Plant rhizodeposition—An important source for carbon turnover in soils. *J. Plant Nutr. Soil Sci.* **2002**, *165*, 397–408.
- (25) Kuzyakov, Y.; Demin, V. CO₂ efflux by rapid decomposition of low molecular organic substances in soils. *Sci. Soils* **1998**, *3*, 2.
- (26) Drever, J. I. The geochemistry of natural waters. In *Surface and Groundwater Environments*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1997.
- (27) van Hees, P. A. W.; Jones, D. L.; Godbold, D. L. Biodegradation of low molecular weight organic acids in coniferous forest podzolic soils. *Soil Biol. Biochem.* **2002**, *34*, 1261–1272.
- (28) van Hees, P. A. W.; Lundström, U. S.; Giesler, R. Low molecular weight organic acids and their Al-complexes in soil solution—Composition, distribution and seasonal variation in three podzolized soils. *Geoderma* **2000**, *94*, 173–200.
- (29) Roelofs, R. F. R.; Rengel, Z.; Cawthray, G. R.; Dixon, K. W.; Lambers, H. Exudation of carboxylates in Australian Proteaceae: chemical composition. *Plant, Cell Environ.* **2001**, *24*, 891–903.
- (30) Qin, R.; Hirano, Y.; Brunner, I. Exudation of organic acid anions from poplar roots after exposure to Al, Cu and Zn. *Tree Physiol.* **2007**, *27*, 313–320.
- (31) Das, A.; Krishnaswami, S.; Bhattacharya, S. K. Carbon isotope ratio of dissolved inorganic carbon (DIC) in rivers draining the Deccan Traps, India: Sources of DIC and their magnitudes. *Earth Planet. Sci. Lett.* **2005**, *236*, 419–429.
- (32) Gislason, S. R.; Arnórsson, S.; Ármannsson, H. Chemical weathering of basalt in southwest Iceland: effects of runoff, age of rocks and vegetative/glacial cover. *Am. J. Sci.* **1996**, *296*, 837–907.
- (33) Andrews, J. A.; Schlesinger, W. H. Soil CO₂ dynamics, acidification, and chemical weathering in a temperate forest with experimental CO₂ enrichment. *Global Biogeochem. Cycles* **2001**, *15*, 149–162.
- (34) Albough, T. J.; Allen, H. L.; Kress, L. W. Root and stem partitioning of *Pinus taeda*. *Trees* **2006**, *20*, 176–185.
- (35) Dormaar, J. F.; Naeth, M. A.; Willms, W. D.; Chanasyk, D. S. Effect of native prairie, crested wheatgrass (*Agropyron cristatum* (L.) Gaertn.) and Russian wildrye (*Elymus junceus* Fisch.) on soil chemical properties. *J. Range Manage.* **1995**, *48*, 258–263.
- (36) Robbins, C. W. Carbon Dioxide Partial Pressure in Lysimeter Soils. *Agron. J.* **1986**, *78*, 151–158.
- (37) Palandri, J. L.; Kharaka, Y. K. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling; U.S. Geological Survey Open File Report 2004–1068: Menlo Park, 2004.
- (38) Bullard, J. W.; Enjolras, E.; George, W. L.; Satterfield, S. G.; Terrill, J. E. A parallel reaction-transport model applied to cement hydration and microstructure development. *Modell. Simul. Mater. Sci. Eng.* **2010**, *18*, 025007.
- (39) Nezat, C. A.; Blum, J. D.; Klaue, A.; Johnson, C. E.; Siccama, T. G. Influence of landscape position and vegetation on long-term weathering rates at the Hubbard Brook Experimental Forest, New Hampshire, USA. *Geochim. Cosmochim. Acta* **2004**, *68*, 3065–3078.
- (40) Curtis, C. D. Stability of minerals in surface weathering reactions: a general thermochemical approach. *Earth Surf. Processes* **1976**, *1*, 63–70.
- (41) Durand, N.; Gunnell, Y.; Curmi, P.; Ahmad, S. M. Pedogenic carbonates on Precambrian silicate rocks in South India: origin and paleoclimatic significance. *Quat. Int.* **2007**, *162*–163, 35–49.
- (42) Jenny, H. *Factors of Soil Formation*; McGraw-Hill: New York, 1941.
- (43) Schaefer, T. D.; McGrail, B. P. Dissolution of Columbia River Basalt under mildly acidic conditions as a function of temperature: Experimental results relevant to the geological sequestration of carbon dioxide. *Appl. Geochem.* **2009**, *24*, 980–987.
- (44) Bryan, S. E.; Ernst, R. E. Revised definition of large igneous provinces (LIPs). *Earth-Sci. Rev.* **2008**, *86*, 175–202.
- (45) Wiseman, I. M.; Edwards, P. J. Constructed wetlands for minewater treatment: Performance and sustainability. *Water Environ. J.* **2004**, *18*, 127–132.