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OPINION

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Soil carbon management and enhanced rock weathering: The separate fates of organic and inorganic carbon

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Abstract

Soil carbon (C) management has been promoted as one of the few readily available strategies to mitigate the rising concentration of atmospheric CO_2 and its associated impacts on climate change. One of these carbon management strategies is enhanced rock weathering (ERW) which involves adding crushed silicate rocks to the soil. These rocks weather and remove atmospheric CO_2 by converting it into bicarbonate in solution. The approach requires careful interpretation of the differences between soil organic carbon (SOC) and soil inorganic carbon (SIC) and their measurement, with implications for land management and C credit accounting. In this Opinion, we emphasise the distinct nature and fates of SOC and SIC, advocating for their separate management, particularly in C credit schemes. It is imperative that protocols for soil C management explicitly recognise the difference between SOC and SIC to prevent any ambiguity. Farmers should be able to claim credits for increases in SOC alongside and independently of any claim for credits for ERW (i.e. SIC). Despite the potential of ERW for C removal, we emphasise that further research is needed to improve the measurement and monitoring of SIC and to understand ERW's potential implications for SOC turnover and greenhouse gas emissions.

Highlights

- Enhanced Rock Weathering increases dissolved inorganic carbon (bicarbonate).
- Soil organic carbon (SOC) may be influenced by Enhanced Rock Weathering.
- Carbon credit via Enhanced Rock Weathering is separate from credit linked to soil organic carbon.
- Soil organic matter and enhanced rock weathering both have roles to play for carbon credits.

KEYWORDS

agriculture, carbon, enhanced rock weathering, greenhouse gas emissions, interventions, soil organic matter

1 | INTRODUCTION

Soil carbon (C) plays a vital role in the global C cycle (Lal, 2003) acting at the interface between the atmosphere and the geosphere. The total quantity of C held within soil, referred to as the soil C stock, comprises two major components: soil organic carbon (SOC) and soil inorganic carbon (SIC). SOC, the most abundant terrestrial C pool (approx. 1550 Pg), is primarily a component of soil organic matter (SOM), while SIC, the smaller portion of C in soils (approx. 950 Pg), mainly consists of carbonates derived from geological or soil parent material sources (Trumper et al., 2009).

Briefly, photosynthesis removes CO_2 from the atmosphere, incorporating C into plant biomass and via plant growth into the soil (in organic forms, i.e. SOC). The C in plant biomass is transformed through complex interactions with animals and microbes, eventually becoming part of the SOM. The decomposition of SOM results in some of the SOC being released as CO_2, while a portion contributes to further increments of SOC stock. By contrast, although the SIC stock is primarily derived from geological sources, the decomposition of SOM and the release of CO_2 into the soil pore space can lead to the formation of bicarbonate in solution, which may precipitate as pedogenic carbonate minerals (Manning, 2008; Washbourne et al., 2015). The soil solution is mobile, draining to recharge groundwater (Gastmans et al., 2016) or entering surface waters and ultimately reaching the sea. Storage of inorganic C as bicarbonate in solution is often overlooked as a component of SIC.

Effective soil C management needs to consider both SOC and SIC, and is crucial for climate change mitigation (IPCC, 2018; Royal Society and Royal Academy of Engineering, 2018). The '4 per mille' initiative (Minasny et al., 2017) highlights the importance of managing land to increase SOM contents, as a nature-based process that removes CO_2 from the atmosphere. In this sense, techniques such as the incorporation of crop residues and no-till practices, among many others, have demonstrated a strong capability to increase SOC. Although valuable and necessary from various perspectives (e.g. improving soil health, water quality, crop productivity, etc.), the effectiveness in long-term CO_2 removal as SOC is challenging. This is because a large part of the SOC is subjected to decomposition processes and 'turns over' (Baveye et al., 2023) unless stabilised by transformation into biochar or aggregates with soil minerals that protect the organic matter. In many cases, and for a portion of SOC, this represents only temporary C storage rather than 'permanent' sequestration.

In recent years, the process of ERW has gained attention as another way of removing atmospheric CO_2, through the production of bicarbonate (i.e. SIC) in solution. This process removes CO_2 from the biological C cycle, facilitating potential long-term C storage in groundwater and surface waters (Gastmans et al., 2016). The process involves the application of an appropriate crushed silicate rock to soil, where weathering products enter the soil solution and, as mobile components of this, are transported away from the site of application.

While the management of SOC is well known to farmers and other landowners, extending that to the management of SIC is a more challenging task, informed by rapidly developing research. Deployment of this knowledge in practice involves a steep learning curve, particularly for ERW. Such knowledge could benefit not only farmers, but also other landowners with the potential capability to build stocks of soil C in their estates (for example, the UK's Ministry of Defence manages an estate over 433,000 ha, and the creation of green infrastructure in engineering projects uses large amounts of silicate rocks). We consider that the extension beyond agriculture to this broad community could be essential if soil C management is truly going to be useful in mitigating the effects of increased atmospheric CO_2.

The purpose of this Opinion is to emphasise the distinct nature and potential fates of SOC and SIC, and, in this context, to discuss potential implications for soil C management and the use of ERW, as well as the trading of C credits.

2 | SOIL ORGANIC CARBON (SOC) AND SOIL INORGANIC CARBON (SIC) NATURE AND FATES

2.1 | Soil organic carbon

Organic materials at different stages of decomposition comprise what we know as SOM, which is typically estimated to be 1.724 times the amount of SOC (Pribyl, 2010). Materials that contain SOC include crop residues, plant tissue, decomposed detritus, animal remains, living components like roots (and their exudates), soil organisms of various sizes and their metabolic products. Chemically, besides C, the compounds that make up SOM contain a wide range of different elements, including hydrogen, oxygen, nitrogen, phosphorus and sulphur. The factor of 1.724 represents the ratio of an assumed value for the relative molecular mass of SOM to the relative atomic mass of C, and therefore, given its high heterogeneity, it represents a general approximation with different studies suggesting a theoretical range between 1.4 and 2.5. Pribyl (2010) suggests a value of 2 is taken, and notes that there are other sources of error in the determination of SOM through the combustion method, which assumes that weight loss at typically 450°C corresponds to the SOM content; some clays also lose weight when heated to this temperature (for example, gibbsite loses 7.4% of its weight at 222°C and 22.1% at 303°C; Balek et al. (2003)).

Due to its high heterogeneity, SOC storage originating from SOM comprises pools with varying stabilities and residence times (Dungait et al., 2012). Many factors can influence the stability and residence time of SOC, including the chemical and physical nature of the input material, soil properties such as texture, biological activities and community composition, environmental conditions, quantities of SOM input, etc. (Dixon et al., 1994; Trumbore, 1997). In simple terms, its decomposition is governed by various biological, physicochemical, and structural factors, including its isolation from microbes, soil aggregation and physical protection, as well as chemical recalcitrance. Historically, it has been suggested that simple organic compounds (such as sugars, amino acids and starch, and carboxylic acids as in plant root exudates) are readily accessible substrates for microbial metabolism, and are thus rapidly decomposed, or 'labile'. Conversely, more complex organic compounds, ranging from polysaccharides to polymeric materials such as lignins, waxes and humic substances, are considered more stable or 'refractory' with greater polymerisation and aromatisation. This has led to the so-called macromolecules concept, where stabilised SOM results from the gradual condensation of plant molecules and their decomposition products. Stability is also influenced by the C:N ratio, and biochemical recalcitrance of input material (expressed by the ratio lignin:N).

While these concepts are important, recent studies have challenged them by indicating: (i) rather than macromolecules, the SOM biotransformation results in supramolecular products, i.e. a group of small molecules that are interconnected via weak bonds (e.g. hydrogen bonds or hydrophobic interactions), (ii) soil microbial communities can degrade even the so-called recalcitrant C forms, and (iii) labile C forms can contribute to the preservation of more stable fractions (Basile-Doelsch et al., 2020; Kleber et al., 2011; Lehmann & Kleber, 2015; Lützow et al., 2006). Thus, SOM stabilisation and long-term SOC storage primarily occur through mechanisms such as physical and chemical protection, including the sorption of C into fine soil particles (silt and clay), the mineral associated organic matter fraction (MAOM, Lavallee et al., 2020) the occlusion/transformation of the SOM by microbial activities, and its association with soil minerals (Amelung et al., 2020; Dungait et al., 2012; Lal et al., 2015; Marschner et al., 2008; Schmidt et al., 2011). In these cases, spatial inaccessibility and interactions with mineral surfaces play an important role in the stabilisation processes (Lützow et al., 2006; Six et al., 2002; Sollins et al., 1996).

Regardless of the process, the literature provides us with one certainty: capturing SOC for climate mitigation goals is important and feasible, but providing it with a precise stabilisation time remains a challenging task that still requires further investigation.

2.2 | Soil inorganic carbon

Inorganic C in the soil (i.e. SIC) primarily occurs as the carbonate mineral calcite ($CaCO_3$; Rawlins et al. (2011)). This has two sources: inherited geological carbonate, derived from limestones and other geological materials, and pedogenic carbonates, which form within the soil and can be recognised on the basis of the carbon and oxygen stable isotopic composition (Cerling, 1984). Jenny (1941b) elegantly describes the occurrence of pedogenic carbonates in the context of rainfall. They occur predominantly in areas of low rainfall, and at depths in the soil profile that increase with increasing rainfall. Using the relationship shown by Jenny (1941a), in the UK (because of high rainfall) pedogenic carbonates would be expected at depths greater than 1 m. Deeper pedogenic carbonates will not be recognised in a conventional soil survey that is restricted to depths less than 1 m. However, pedogenic carbonates have been recognised in Technosols in urban areas of the UK, a modern age confirmed by ^{14}C dating (Washbourne et al., 2015), and in artificial soil blends (Manning et al., 2013). In addition to forming by direct precipitation from the soil solution, pedogenic carbonates are formed in the gut of earthworms and are excreted into the soil (Bossuyt et al., 2004; Lambkin et al., 2011; Zhang et al., 2013). Pedogenic carbonates also form through the decomposition of calcium oxalate minerals (e.g. whewellite, $CaC_2O_4.2H_2O$) that are produced by plants and fungi (Gadd et al., 2014). Within the soil system, the organic oxalate component is oxidised to form carbonate, as calcite. This process is important in some tropical systems, such as soils associated with the Iroko tree (Gatz-Miller et al., 2022).

An additional form of inorganic C arises from the accumulation of bicarbonate in solution, as a consequence of natural weathering processes (elaborated upon in greater detail in Section 3). However, owing to its mobility and absence of retention within the soil matrix, this is often overlooked (i.e. not considered as SIC). It is at the heart of the enhanced rock weathering process, opening up a new need to understand its origin, amount, and fate.

3 | ENHANCED ROCK WEATHERING

3.1 | Principles

Enhanced Rock Weathering (ERW) involves the addition of crushed silicate rocks to the soil (Goll et al., 2021), enhancing weathering rates by increasing the reactive surface area and exposing the crushed rock to bioweathering in the surficial soil horizons. The ability of crushed silicate rock to act as a source of crop nutrients has been recognised for over a century (e.g. Ciceri et al., 2015 and Winiwarter & Blum, 2008). Attention is currently focusing on minerals, and rocks that contain silicate minerals, that weather rapidly based on the empirical observations of Goldich (1938), which have a thermodynamic basis as demonstrated by Curtis (1976).

The weathering process of silicate rocks releases cations due to the hydrolysis of the mineral's polymeric aluminosilicate or silicate crystal lattice. The hydrolysis results in the formation of electrically neutral OH species, such as $Si(OH)_4$ in solution, and in most near-neutral low pH soils, clays and Fe,Al oxyhydroxide minerals also form. The process releases cations, and in the absence of artificial acid inputs, the anion in solution that counterbalances these is bicarbonate, ultimately, in soils, of biological origin.

A number of studies have shown that weathering involves the formation of bicarbonate in solution, which can then enter groundwater and surface waters. Carbon and oxygen stable isotope studies of pedogenic carbonate minerals have shown that their isotopic characteristics directly relate to a photosynthetic origin and, in some cases, a specific pathway (C3 or C4). This has enabled, for example, prehistoric changes in vegetation type to be determined (Cerling et al., 1997; Durand et al., 2007; Salomons et al., 1978; Salomons & Mook, 1976). Secondly, elegant work by Moulton et al. (2000) to compare groundwater compositions for vegetated and non-vegetated slopes on basaltic rock in Iceland clearly showed an increase in bicarbonate under trees, and that the bicarbonate migrated via a hydrogeological system. Similarly, Taylor et al. (2021) demonstrate that the application of the calcium silicate mineral wollastonite ($CaSiO_3$) to the Hubbard Brook Forest catchment, New Hampshire, led to measurable increases in bicarbonate in catchment waters. Third, as recognised by Chebotarev (1955a, 1955b) for the Australian Great Artesian Basin, the dominant anion in groundwaters closest to the surface is bicarbonate, as seen in the analysis declared on the side of any purchased bottled water. Importantly, a detailed study of basaltic aquifers in Brazil (Gastmans et al., 2016), which provide a safe public water supply for many millions of people, concluded that natural weathering processes involve bicarbonate as the dissolved anion, other anions occurring as a consequence of man-made pollution.

In summary, building on these independent observations of the role of rock weathering in removing atmospheric CO_2, many specific studies have been designed to measure the weathering process in the context of ERW and its deployment, which are then calibrated against geochemical models predicting CO_2 removal rates (Section 3.4).

3.2 | Estimation of potential CO_2 removal

The amount of CO_2 that can potentially be captured through the formation of charge-balancing bicarbonate is directly related to the cation content of the silicate rock that is used. The dominant cations are Ca, Mg, Na, and K. It is assumed that Fe within the crushed rock does not contribute to CO_2 removal in solution, as it is fully oxidised during weathering on or near the soil surface to produce Fe-oxyhydroxide minerals, as seen in mottled and gley soils in temperate climates, and widely in red tropical soils. Similarly, at near-neutral pH, Al is immobile in the soil environment, forming clays and Al-oxyhydroxide minerals (Hudson, 1995).

The starting point for estimation of potential CO_2 removal is based on a conventional whole-rock analysis, determined by X-ray fluorescence analysis of the solid rock, or analysis of a solution of the rock following dissolution in strong acids using inductively coupled plasma (ICP) techniques. An example of an analysis, as reported in the literature, is given in Table 1.

Using the data given in Table 1, the total number of moles of Ca, Mg, Na, and K is calculated and expressed as moles of positive charge, subtracting Ca present in the rock as apatite ($Ca_5(PO_4)_3OH$), which does not contribute to ERW as its congruent dissolution involves release of the phosphate anion. The total positive charge from the cations derived from silicate minerals requires an equal number of moles of bicarbonate to maintain electrical neutrality in the solution. Table 2 presents this calculation for the rock analysis given in Table 1 and represents the maximum possible CO_2 removal for a specific rock.

TABLE 1 Chemical composition of 3 representative samples of dolerite. Data were taken from Randall (1989), for Barrasford Quarry, Northumberland, UK. Fe is separately determined as Fe^{2+} and Fe^{3+}. H_2O^+ denotes water lost above 110°C, and so relates to hydroxide in minerals such as clays, micas, and amphiboles.

	Wt%	*Wt%*	*Wt%*
SiO_2	49.50	50.20	50.50
TiO_2	2.36	2.20	2.16
Al_2O_3	14.43	13.90	13.80
Fe_2O_3	3.82	4.79	3.46
FeO	8.51	7.99	8.96
MnO	0.19	0.17	0.17
MgO	6.12	5.90	5.89
CaO	9.36	9.30	9.55
Na_2O	2.42	2.41	2.55
K_2O	0.95	0.90	0.77
P_2O_5	0.29	0.26	0.32
H_2O^+	1.33	1.28	1.88
S	-	0.10	0.10
Total	99.28	99.40	100.11

An alternative to the determination of charge balance is to use the Steinour equation (Equation (1)), as modified by Renforth (2019):

$$\mathrm{erwCO_2} = \frac{44}{100}.\left(\frac{CaO}{56}+\frac{MgO}{40}+\frac{Na_2O}{62}+\frac{K_2O}{94}-\frac{SO_3}{80}-\frac{P_2O_5}{142}\right).10^3.1.5 \tag{1}$$

In this, the oxide wt% content is converted to molarity, and a correction is made for sulfate and phosphate, which occur in some rocks combined with Ca in minerals such as gypsum ($CaSO_4.2H_2O$) or apatite ($Ca_5(PO_4)_3OH$). These corrections can be neglected for the majority of igneous rocks, as the S and P contents are very low, and in any case, the equation as published by Renforth (2019) does not take into account the stoichiometric proportion of Ca associated with P. The final coefficient of 1.5 reflects inefficiencies in the process of transport to the ocean; various studies suggest that the coefficient varies between 1.4 and 1.7, with a value of 1.5 taken as a conservative estimate (Renforth, 2019).

Having calculated the CO_2 that can be removed through ERW of silicate rock, the potential benefit of using a particular rock can be determined in terms of C removal, and compared from one rock to another. The calculation results presented in Table 2 represent the maximum amount of CO_2 that can be obtained through complete weathering of the rock.

TABLE 2 Recalculation of dolerite analyses to estimate CO_2 removal, based on charge balance and (last line) using the modified Steinour equation from Renforth (2019). For charge balance, correction is made for Ca bound to phosphate in apatite ($Ca_5(PO_4)_3OH$) assuming 5 moles of Ca equivalent to 3 moles of phosphate. S is assumed to be present as sulphide minerals (Randall, 1989), hence not bound to Ca and so no correction has been made.

Moles oxide				
MgO		0.153	0.148	0.147
CaO		0.167	0.166	0.171
Na_2O		0.039	0.039	0.041
K_2O		0.010	0.010	0.008
P_2O_5		0.002	0.002	0.002
Moles charge				
Mg^{2+}		0.306	0.295	0.295
Ca^{2+}		0.334	0.332	0.341
Na^+		0.078	0.078	0.082
K^+		0.020	0.019	0.016
Ca (apatite correction)		−0.003	−0.003	−0.004
Total		0.735	0.721	0.730
Moles HCO_3^-		0.735	0.721	0.730
g CO_2/100 g		32.35	31.72	32.14
	kg $tonne^{-1}$	323	317	321
Steinour Eq.:				
Renforth (2019)				
ERW	kg $tonne^{-1}$	242	237	240

The rate of weathering is much more difficult to estimate.

3.3 | Costs

The financial cost of producing crushed rocks suitable for ERW is surprisingly low, because the quarrying industry is highly mechanised and extremely energy and labour efficient, given the need for it to supply very large quantities of crushed rock for competitive construction markets. The United States Geological Survey estimates an average price of US$ 14 per tonne for US production of 1.5 billion tonnes annually (USGS, 2022). European annual production of crushed rock is 1.3 billion tonnes (Idoine et al., 2023). World production of crushed rock can be estimated using the per capita consumption figures for Europe (2.8 tonnes per person) and the USA (4.5 tonnes per person), and so is of the order of 22–36 billion tonnes annually. It is important to bear in mind that these statistics are for all crushed rocks, and so include limestone and other rocks that play no role in ERW. There are no rigorous published statistics for national or multinational production that distinguish silicate rocks from limestone, but a reasonable estimate would be 20% of the total (Mankelow et al., 2021; USGS, 2022).

The process of crushing silicate rocks necessarily generates 'fines', typically material below 4 or 5 mm in size. For every tonne of rock product, typically 250–300 kg of fines is produced (Mitchell et al., 2006). Thus, the amount of fines produced annually by the construction sector is of the order of 300 million tonnes in the USA, 260 million tonnes in the EU, and 4–7 billion tonnes globally, of which approximately 20% could be considered for ERW, derived from existing mining activity.

An estimate of the C cost of producing crushed basalt has been made by Lefebvre et al. (2019), for São Paulo state, Brazil. The market for equipment used for this purpose is global, so the results of this study are widely transferable. This study reports that crushing requires approximately 5 kg CO_2 (assuming fossil fuels are used to generate the required electricity) per tonne of rock. Lefebvre et al. (2019) concluded that a typical basalt could be transported over 900 km before the C cost of production, transport and spreading was greater than the benefit of CO_2 removal. Further investigations, however, are still needed, particularly considering different types of rocks and locations where alternative sources of electricity might be used in the process. For instance, the distinction between fossil fuel and hydroelectric power usage, as observed in Brazilian quarries, warrants examination, and could lead to lower embedded carbon for products of crushing operations that use 'green' electricity.

3.4 | Complications

The amount of CO_2 removed as a consequence of ERW depends on many factors. To evaluate the potential CO_2 removal, the assumption is made that the rock analysis reflects a pristine, unweathered, silicate rock. In practice, this may not be achieved, for two reasons. First, prior to quarrying, the rock may already have undergone some weathering to produce clays, or hydrothermal carbonation to produce calcite before exposure at the surface. Secondly, the material that is crushed may include a small amount of sedimentary rock, if this also occurs in the quarry. If either of these has happened, the chemical analysis of the quarry fines derived from the crushing plant will include material that cannot weather through the ERW process, and so the CO_2 removal will be overestimated. A simple indication of whether or not this problem needs attention is to refer to the Loss on Ignition (Table 1), determined typically at 1000°C, which reports the weight loss due to decomposition of carbonate minerals and clays. A further complication is that it is rare for modern routine analysis of silicate rocks to distinguish Fe^{2+} from Fe^{3+} (Table 1), normally reporting simply as total iron expressed as Fe_2O_3. This shortcoming does not affect the estimation of CO_2 removal, but it may be important when considering rates of reaction, because these can be influenced by the oxidation of Fe^{2+} during weathering.

Although it is relatively easy to calculate the potential total amount of CO_2 involved in the weathering reaction, it is much more difficult to determine the rate of the weathering reaction. This is necessary to predict rates of CO_2 removal and to decide when the added crushed rock has been completely weathered, and so when further applications may be made following the exhaustion of earlier applications. To do this requires modelling of the weathering process, which in turn requires knowledge of the dissolution rates for the individual minerals within the rock, their proportions, and their relative surface areas once crushed. Such models are calibrated against experiments, as carried out by Kelland et al. (2020). However, our knowledge of the mineral dissolution rates, although compiled in an internally consistent format (Heřmanská et al., 2022, 2023; Palandri & Kharaka, 2004), is based on data from a very wide range of studies carried out mainly in the final quarter of the 20th Century that, in many cases, focused on subsurface environments relating to the needs of the petroleum industry to model sediment diagenesis (e.g. Oelkers et al., 2000).

3.5 | Implications for biological processes

As discussed by Vicca et al. (2022) and Dupla et al. (2023), it is important to evaluate the impact of ERW on biological processes to make sure the increase in SIC would not have a negative effect, which could culminate in a higher impact on biodiversity and climate change. Calogiuri et al. (2023) designed and constructed an experimental setup for ERW rates through soil organisms while concurrently controlling abiotic conditions, and considered the role of earthworms in ERW (Calogiuri et al., 2023). Despite the difficulties inherent in predicting mineral dissolution rates, there may be an increase in plant growth after the application of crushed rock, which in turn result in enhanced SOM inputs. Manning (2022) demonstrates how the release of silica from mineral weathering is able to meet what is taken up by a growing crop of wheat, and that the silica has to be derived from silicate minerals and not quartz (SiO_2), which is an inert residual product of the weathering process. Other studies also found an increase in productivity after applying basalt; Vienne et al. (2022) and Reynaert et al. (2023) found an improvement in forage productivity after the application of basalt under a persistent rainfall regime.

An additional complication concerns the uncertain consequences on SOC sequestration and greenhouse gas (GHG) emissions from soils treated with rock dust. To date, there is very little documentation (not published in peer-reviewed literature and still limited) on the potential implications of rock dust application for GHG emissions. This is critical and merits special attention from researchers. Initial reports indicate mixed results, particularly for CO_2 fluxes in short-term assessments. Some studies indicate increased CO_2 fluxes, while others report no increase or even reductions (i.e. CO_2 removal). Furthermore, an evaluation of implications on other GHGs (e.g. N_2O, which is about 300 times as potent as CO_2) appears to be lacking. ERW can affect soil pH, giving a small increase in pH (Skov et al., 2024) or potentially decreasing pH if sulfide minerals are present in the rock as these weather to produce sulfuric acid. Changes in pH may increase N_2O emissions from soil in the long term due to an increase in denitrification and/or change in denitrifying communities in the soil (Baggs et al., 2010). In one empirical study assessing the effects of crushed basalt rock application on N_2O emissions (Chiaravalloti et al., 2023), the authors observed a decrease in N_2O emissions from the soil, using a mesocosm setting with maize, which could be a highly favourable outcome when it comes to climate mitigation purposes. However, another study found an increase in N_2O fluxes after basalt application during irrigation events (Poblador et al., 2022). These contrasting studies emphasise the requirement for further research using other rock types and more "real-world" scenarios (i.e. field experiments).

4 | MEASUREMENT AND MONITORING

The different forms of soil C (i.e. SOC and SIC) can be distinguished using thermal analysis (Lopez-Capel et al., 2005), especially when combined with analysis of the evolved gases (Lopez-Capel et al., 2006). On heating in air or an oxidising mix of gases, labile organic C such as cellulose, decomposes at temperatures around 350°C, and more stable organic C such as lignin at around

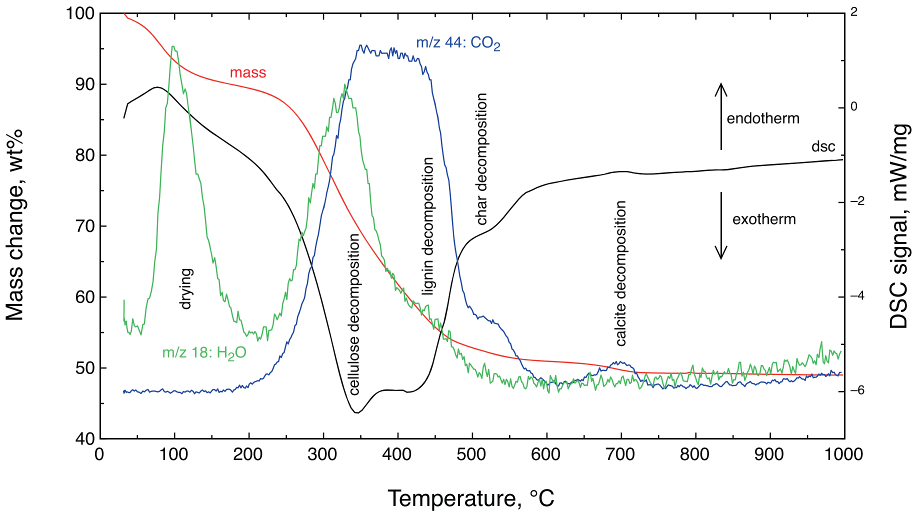

FIGURE 1 TG-DSC-QMS traces (run in 80% He, 20% O_2) for wormcast from silty loam soil developed on dolerite, Northumberland, UK, showing (a) mass loss (red), (b) sample energy input/output (DSC; black), and evolved gases: (c) m/z 18: H_2O (green), and (d) m/z 44: CO_2 (blue). Note initial endothermic drying (c. 100°C), exothermic decomposition of cellulosic material (empirical formula CH_2O; c. 350°C), exothermic decomposition of lignin-like material (c. 450°C) and char (c. 500°C), then endothermic decomposition of calcite (700°C). Events based on Lopez-Capel et al. (2005).

450°C. Inert C, such as charred material, typically decomposes at 550°C. As an example, Figure 1 shows a trace for a wormcast from a silty loam from NE England, in which the different types of C can be distinguished.

More recently, Zani et al. (2023) also applied the same technique to assess different types of C under different farming systems, which shows the broad range and the power of such an approach. However, although TG-DSC-QMS is considered a very powerful tool for characterising SOM, it is not suitable for routine determination of soil C contents, especially when statistical analysis is required. This is largely because of two reasons: first, each analysis can take up to two hours to complete the heating cycle, so sample throughput is slow. Secondly, the small sample size (typically 30 mg; Lopez-Capel et al. (2005)) means that there are challenges extrapolating to the field scale. Instead, the technique provides valuable insights into the types and quality of SOM and minerals that are present, complementing techniques such as X-ray diffraction.

In practice, the determination of the C content (Nelson & Sommers, 1996) of suitably prepared soil samples conventionally involves the analysis of total C, total SOC, and total SIC. Historically, wet chemical methods have been used that involve the complete oxidation of organic C using potassium dichromate solutions, thus determining SOC (Walkley, 1947; Walkley & Black, 1934). Where resources allow, these have largely been superseded through the wide use of instrumental methods of C determination (Chatterjee et al., 2009). Thermal analysis provides a basis for understanding the function of modern instrumental methods designed to handle large numbers of bulk samples. Typically, the sample is heated (with a catalyst in some systems) until it decomposes completely, measuring the CO_2 that has been produced either for the entire heating run, or for stages that correspond to the different forms of SOC (Figure 1). This gives a direct measurement of total C if combustion is carried out at temperatures high enough (typically 1000°C) to completely decompose carbonate minerals.

In cases where only total C can be measured, the sample is first run without chemical treatment, then a second sample that has been treated with acid to remove carbonates is analysed to measure SOC. SIC is then determined by difference, compounding the analytical error inherent to the technique. SIC can be determined directly through calcimetry or other methods that involve acid digestion and measurement of the evolved CO_2. In other instrumentation that is designed to determine the amounts of CO_2 evolved for specific temperature intervals during a heating profile (similar to that shown in Figure 1), direct and independent determination of SOC and SIC is possible. This gives the most accurate determination of SIC, especially for low concentrations, as it avoids the error inherent in estimating by difference, as well as problems that may arise in chemical treatment to remove carbonates. Because of the speed of analysis, the availability of autosamplers and the reduction in human error, many commercial laboratories offer instrumental determination of soil C contents. Some offer direct determination of SIC using instruments capable of distinguishing different temperature ranges in a heating profile.

While all of the aforementioned factors are significant for SOC and SIC, measuring the accumulation of the latter from ERW presents challenges due to the transfer of inorganic C as bicarbonate in solution. As previously mentioned, this bicarbonate can migrate with the soil solution down hydrological gradients to enter surface water systems and eventually reach the ocean or groundwater. This has obviously direct implications for monitoring procedures. Given its nature, ERW operates within an open system, operating conceptually on a global scale. The flux of C away from the location of rock weathering, with dilution and dispersion as a natural consequence of hydrological and hydrogeological processes, complicates measurements and attribution to specific interventions.

Nonetheless, studies of the effects of ERW typically involve two approaches: determination of increases in the bicarbonate concentration of the soil solution (measured as alkalinity; Kelland et al., 2020), or chemical analysis of the soil to show removal of the crushed rock (Reershemius et al., 2023). Measurement of solution alkalinity requires collection of the soil solution, either from field samplers or from mesocosms in which the solution has flowed through a column of soil to a drainage collection point (Zani et al., 2024). Changes over time in solution bicarbonate and cation content are used to calibrate geochemical models that predict the release of cations based on the rates of weathering reactions, and so the rate of removal of atmospheric CO_2 as a consequence of the application of crushed rock to soil. Direct measurement of the removal of crushed rock through weathering depends on very precise determination of changes in soil composition relative to 'immobile' elements such as Ti, and currently depends on access to university research laboratories with Class 10 clean-room sample preparation facilities and highly sensitive analytical techniques (isotope dilution inductively couple plasma – mass spectrometry; Reershemius et al. (2023)). Hence, quantifying CO_2 removal by ERW, using either approach, requires a wide range of expertise and competencies in petrology, geochemistry, soil physics, hydrology, and hydrogeology, making it a highly challenging task.

5 | IMPLICATIONS FOR LAND MANAGEMENT

To claim credits for soil C management, land managers must be able to measure the effects of their interventions and track changes over time. Protocols based on SOM are well established (although there is always room for improvement) and relatively accessible. Often, they involve the calculation of the soil C stock through a rigorous approach, such as the method outlined by Zani et al. (2021), where soil samples are collected in a determined way, processed appropriately, and analysed using widely available and long-established techniques. Long-term changes are also predicted using mechanistic biogeochemical models that are more long standing (e.g. RothC, Daycent, Century, DNDC, ECOSSE, etc.).

While existing protocols based on SOM and SOC are quite thorough, they need to be supplemented to encompass ERW. Changes in SOC need to be known, so these can be measured in the same manner as in the management of SOM. As previously discussed, measurement of SIC as bicarbonate in solution cannot be done using traditional soil sampling and analytical methods. Additionally, existing mechanistic biogeochemical models developed for SOM and SOC are not yet equipped to predict SIC as bicarbonate. In this sense, to be accepted for C trading purposes, ERW protocols must include several discrete activities, including: (1) evaluation of the potential for CO_2 removal for a specific rock type; (2) conducting a C life cycle analysis for each case of rock application (including transportation from source to destination); and (3) performing geochemical modelling of CO_2 removal for weathering of each specific rock, calibrated through experiments. Each of these individual steps requires research expertise in different disciplines, at a level of university or government research institutes. Companies capable of combining this level of expertise are beginning to emerge.

The key point is that measurement of CO_2 removal by ERW is not something that most single farming businesses can do at this point in time – it is simply too expensive to employ the required skills, either directly or through a consultancy. By contrast, it is possible for farmers to use existing commercial analytical laboratories to measure and monitor SOC, and hence to measure the response of this to interventions as part of the management of SOM, although this also has a cost that might not be offset by benefits in the form of subsidies. To illustrate some of the complexities in managing soil carbon, Tyllianakis et al. (2023) assess land managers' attitudes to agri-environmental schemes that focus on C, but does not state that the study relates specifically to SOC, and does not consider ERW.

6 | FINAL REMARKS

The purpose of this Opinion is to provide an overview based on the existing peer-reviewed literature regarding the distinct nature and fate of SOC and SIC. We advocate for the importance of considering both forms of carbon in any future soil management plans aimed at removing atmospheric CO_2. Notably, there are many key research gaps; for instance, at the time of writing, reports on GHG emissions measurements from ERW projects are just beginning to appear as abstracts for conference papers and posters (e.g. Scherer et al. (2022)).

Overall, the management of SOC is well established, with the necessary commercial infrastructure and methodologies available to facilitate its accessibility to a wide range of land managers. However, it is crucial that advice, protocols, and guidance concerning SOC must explicitly state (where appropriate) when they do not address SIC or the soil's potential for C capture through ERW.

By contrast, ERW is rapidly developing as a new industry. The protocols associated with ERW must also clarify their stance relating to SOM and SOC, and their rate of accumulation or loss as a consequence of the application of crushed rock to soil. At this stage, the detailed protocol requirements for ERW, which involve many interdisciplinary specialities (including those beyond the existing SOC management, such as life cycle assessment), mean that ERW cannot be monitored and assessed directly by businesses or organisations already challenged by new (UK) agri-environmental schemes. Successful implementation of ERW as a business demands a high level of specialist skills and substantial investment.

Given these differences, the outcome of this Opinion is that SOC and SIC should be managed independently as separate stocks of soil C for C credit purposes, even though they interact directly in nature. This distinction should be clearly stated in documentation and other materials related to soil C management to prevent confusion between the two. There is no scientific reason why farmers should not claim C credits, if they are able to do so, for increases in SOC while allowing independent companies to apply crushed rock to the same land, claiming separate credits according to ERW protocols. These are independent activities.

AUTHOR CONTRIBUTIONS

David A. C. Manning: Conceptualization; writing – original draft; writing – review and editing; resources. **Antonio Carlos de Azevedo:** Conceptualization; writing – review and editing. **Caio Fernandes Zani:** Conceptualization; writing – review and editing. **Arlete

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CONFLICT OF INTEREST STATEMENT

None of the authors have a conflict of interest to disclose.

DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

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