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A Review of Measurement for Quantification of Carbon Dioxide Removal by Enhanced Weathering in Soil

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Abstract

All pathways which limit global temperature rise to <2°C above pre-industrial temperatures now require carbon dioxide removal (CDR) in addition to rapid greenhouse gas emissions reductions. Novel and durable CDR strategies need to rapidly scale over the next few decades in order to reach Paris Agreement Targets. Terrestrial enhanced weathering (EW) involves the acceleration of natural weathering processes via the deployment of crushed rock feedstocks, typically Ca- and Mg-rich silicates, in soils. While models predict this has the potential to remove multiple gigatonnes of CO_2 annually, as an open-system pathway, the measurement (monitoring), reporting, and verification (MRV) of carbon removal and storage is challenging. Here we provide a review of the current literature showing the state-of-play of different methods for monitoring EW. We focus on geochemical characterization of weathering processes at the weathering site itself, acknowledging that the final storage of carbon is largely in the oceans, with potential losses occurring during transfer. There are two main approaches for measuring EW, one focused on solid phase measurements, including exchangeable phases, and the other on the aqueous phase. Additionally, gas phase measurements have been employed to understand CO_2 fluxes, but can be dominated by short-term organic carbon cycling. We stress that, although there is complexity in tracing EW CDR in the natural field environment,

established literature validates existing approaches, and each approach has strengths and limitations. The complexity inherent in open-system CDR pathways is navigable through surplus measurement strategies and well designed experiments, which we highlight are critical in the early stage of the EW CDR industry.

1 Introduction

All emissions pathways which limit global average temperatures to <2ºC now necessitate gigatonne scale removal of atmospheric carbon dioxide (CO_2) in addition to emissions reductions (IPCC, 2022; Smith et al., 2023). In order to meet national and international targets for climate change mitigation, the carbon dioxide removal (CDR) industry has to scale rapidly, delivering high-quality, durable and additional CDR (Campbell et al., 2022; Maesano et al., 2022; Smith et al., 2023). Projected needs for durable CDR range anywhere from 0.06 $GtCO_2$/yr to over 1 $GtCO_2$/yr by 2030, alongside less durable forestation-based methods and land management practices, which is a 30-540 fold increase from 2020 levels of 0.002 $GtCO_2$ (Smith et al., 2023). Accelerating CDR deployment within such a short time frame given the financing, policy, technical and engineering challenges associated with many durable CDR methods highlights the importance of rapidly validating those approaches that are available to scale near-tem and that can readily integrate within existing activity. Much of this validation rests on scientific verification of the net atmospheric CO_2 removed, as well as the assessment of associated environmental impacts. This review addresses the challenge of scientific verification by detailing the current state-of-play of the multiple options for reliably quantifying and monitoring carbon fluxes associated with terrestrial enhanced weathering (EW).

Enhanced weathering is considered a novel CDR technique which aims to speed up chemical weathering of rocks, increasing the flux of dissolved inorganic carbon (DIC, primarily bicarbonate (HCO_3^-)) to the oceans (Seifritz, 1990; Schuiling and Krijgsman, 2006; Köhler et al., 2010; Hartmann et al., 2013; Taylor et al., 2016). The premise of this is that CO_2 dissolved in rain and soil waters as carbonic acid is neutralized by alkaline minerals, generating stable bicarbonate ions in drainage waters which, when transported to the oceans, stored in groundwater reservoirs or precipitated as carbonate minerals in soils become a durable carbon store (Fig. 1).

The global riverine flux of DIC from continental weathering has regulated atmospheric CO_2 on Earth over million year timescales, and currently removes ~1 Gt of CO_2 per year (Walker et al., 1981; Berner and Berner, 2012). In order to speed up this natural process, crushed reactive rocks (e.g., basalt and dunite), minerals (e.g., olivine and wollastonite) or other alkaline materials (e.g., slag, cement kiln dust, or returned concrete) can be applied in agricultural settings (Renforth et al., 2015; Taylor et al.,

2016; Renforth, 2019; Amann et al., 2020; Haque et al., 2020; Kelland et al., 2020; Knapp and Tipper, 2022). Based on generalist model predictions, EW has a global CDR potential in the range of 0.5–4 Gt CO_2 per year (Fuss et al., 2018; Beerling et al., 2020; IPCC, 2022), which can be optimized through the choice of feedstock and weathering environment (Beerling et al., 2020; Cipolla et al., 2021, 2022; Baek et al., 2023; Haque et al., 2023). Such a magnitude of CDR can meaningfully contribute to national and international CDR targets (Taylor et al., 2016; Beerling et al., 2020; Kantzas et al., 2022; Smith et al., 2023) with water and energy requirements lower than most industrial removal technologies (Eufrasio et al., 2022), no required change in land use, all while providing important benefits for crops and communities (Manning and Theodoro, 2020; Swoboda et al., 2022). Moreover, the infrastructure required for deployment already exists.

Enhanced weathering is an open-system CDR pathway and therefore directly monitoring weathering rates, and ultimately calculating net CDR, is challenging. The complexity of this open system presents a significant barrier to scaling the technology (Santos et al., 2023). Under the definition of CDR as a process involving both the capture *and* durable storage of atmospheric carbon dioxide (Smith et al., 2023), the capture phase refers to the formation of bicarbonate at the weathering site with storage occurring primarily as dissolved bicarbonate in the ocean and long lived aquifers (Campbell et al., 2022; Smith et al., 2023) or, less commonly, through the precipitation of carbonate minerals in the soil (Renforth et al., 2009; Haque et al., 2020). Both storage pools are considered permanent by all current carbon management definitions (pedogenic carbonates; ~10^4 years, ocean bicarbonate; ~10^5 years (Berner et al., 1983; Zamanian et al., 2016; Renforth and Henderson, 2017; Kanzaki et al., 2023) but differ in their CDR efficiency with a 50% stoichiometric loss of captured CO_2 occurring during carbonate precipitation (see Campbell et al., 2022).

There are currently numerous approaches to estimating carbon capture at a weathering site, drawn from established soil science, agronomy, geochemistry and geology literature. These approaches can be broadly separated into solid, water and gas based categories. In addition, the use of soil exchangeable cation concentrations presents a hybrid between solid and water based categories, but would be conducted on the samples taken for solid phase analysis. Each category contains multiple geochemical measurement strategies which each have scientific or operational benefits and limitations, with no standard method prevailing in the field (Table 1). Given the nascent phase of EW research and deployment, current crediting methodologies from standard setting bodies allow for a diversity of approaches for CDR quantification (Carbon Standards International (CSI), 2022; Puro.earth, 2022). This methodological framework facilitates operational research and field advancement in the private sector, whilst maintaining social and environmental safeguards. Industrial operations, primarily undertaken through pre-finance agreements, are largely in a research and development phase with the goal of refining methodologies. In parallel, stricter protocols are being

developed based on the best available science which can better ensure robust credit issuance and scientifically responsible operations as the industry grows.

Transport of aqueous bicarbonate through the lithosphere-hydrosphere system occurs post-capture and pre-storage (Fig. 1), often associated with 'downstream' CO_2 losses that decrease CDR efficiency. In order to make a claim for a CDR credit, downstream CO_2 losses should also be quantified as, by the definition above, CDR typically refers to the CO_2 that has been both captured *and* stored. Downstream losses are more difficult to monitor directly compared to capture processes. As such, Earth system models and national riverine monitoring networks may show promise for addressing open system losses (Calabrese et al., 2022; Kanzaki et al., 2022, 2023; Knapp and Tipper, 2022; Zhang et al., 2022; Harrington et al., 2023) but there is currently little industry guidance on how to handle them in CDR claims. Upstream losses (i.e. operational or embodied emissions) must also be quantified by life cycle analysis (Nunes et al., 2014; Lefebvre et al., 2019; Zhang et al., 2023) and included in net-CDR calculations (Carbon Standards International (CSI), 2022; Puro.earth, 2022). We further stress that full assessment of additionality and robust environmental and social safeguarding policies are essential components of responsible EW CDR projects. Many of these safeguards can be incorporated into measurement approaches for quantifying weathering rates and carbon capture.

Carbon removal claims for EW are made based on the enhancement of inorganic carbon cycling, and would typically not include any increased carbon removal by organic carbon pathways, due to the major differences in permanence and durability of the different fractions (Brander et al., 2021). That being said, EW feedstocks may have complex effects on different soil organic carbon fractions, as addition of rock powder may stimulate mineralization of the labile carbon pool, while potentially increasing the long-term stable mineral associated organic matter (Slessarev et al., 2022). As such, whilst we focus on inorganic approaches here, it is important to consider wholescale carbon budgeting approaches to assess the impact of EW on existing carbon management practices, such as soil organic carbon (SOC) storage (Kantola et al., 2023) and wider associated ecosystem carbon removal (Goll et al., 2021).

This review provides an orientation point for EW students, researchers, operators, regulators and wider stakeholders, detailing the basis of current measurement approaches. We outline the current state-of-play and summarize the strengths and limitations of different measurements for EW, primarily focusing on quantification of weathering rates and captured CO_2. We consider downstream CO_2 losses to be beyond the scope of this paper. This review sits alongside a broad review of experimental design strategies (Almaraz et al., 2022), a recent set of thorough analytical recommendations for geochemical carbon dioxide removal (Campbell et al., 2023), and a toolkit developed by CarbonPlan (Holzer et al., 2023b) that outlines system wide considerations for EW.

2 Geochemical tracers for EW

2.1 Overview of the principles of EW and tracing approaches

In its simplest chemical formulation, EW can be considered as an acid–base neutralization reaction. Carbonic acid (containing atmospheric or biogenic CO_2) is neutralized by the dissolution of an alkaline material or mineral, such as a silicate mineral, producing dissolved bicarbonate, dissolved silica, clay minerals and base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). This reaction converts CO_2 dissolved in water to stable bicarbonate ions which are primarily durably stored as dissolved bicarbonate in the ocean or, in a minority of cases, as carbonate minerals. The dissolution of most silicate minerals is incongruent, meaning that mobile cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) are removed via drainage waters, and immobile elements (e.g., Al, Ti) either remain in the soil in recalcitrant minerals or are incorporated into secondary minerals such as clays. These reactions are illustrated in Eq. 1 and 2, showing the dissolution of two idealized feldspar mineral endmembers (anorthite and albite) that are common in silicate rock feedstocks. In this instance, for anorthite, Ca^{2+} and bicarbonate are dissolved in waters, whereas for albite, Na^{+}, bicarbonate and silica are dissolved. In both cases Al and some Si remain in the soil as clay minerals.

$$CaAl_2Si_2O_{8\,(s)} + 2CO_{2(aq)} + 3H_2O_{(l)} \rightarrow Ca^{2+}{}_{(aq)} + 2HCO_{3(aq)}{}^{-} + Al_2Si_2O_5(OH)_{4(s)} \quad (1)$$

$$silicate\ mineral\ (anorthite) + carbon\ dioxide + water \rightarrow calcium + bicarbonate + clay\ (kaolinite)$$

$$2NaAlSi_3O_{8\,(s)} + 2CO_{2(aq)} + 11H_2O_{(l)} \rightarrow 2Na^{+}{}_{(aq)} + 2HCO_{3(aq)}{}^{-} + 4H_4SiO_{4(aq)} + Al_2Si_2O_5(OH)_{4(s)} \quad (2)$$

$$silicate\ mineral\ (albite) + carbon\ dioxide + water \rightarrow sodium + bicarbonate + orthosilicic\ acid + clay\ (kaolinite)$$

A generalized silicate weathering pathway (Fig. 2) illustrates that there are two primary geochemical targets for tracking weathering processes: 1) the constituents of minerals being weathered (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Si), and 2) the carbon consumed or transformed by weathering reactions (CO_2, or HCO_3^{-}) (Almaraz et al., 2022; Amann and Hartmann, 2022). Of these, the former approach is a proxy for mineral dissolution, allowing a calculation of weathering rates and by extension – with significant assumptions – potential carbon capture. The latter provides a more direct measure, but also requires assumptions on mobility and losses.

2.2 Solid phase measurements

2.2.1 Maximum CDR potential of rock powders

An estimate of the maximum CDR potential by EW can be determined using the modified Steinour equation (Steinour, 1959; Renforth, 2012; Renforth, 2019). This is achieved by calculating the amount

of alkali and alkaline cations (wt% of CaO, MgO, Na_2O, K_2O) contained in a rock powder feedstock, and then using charge balance to estimate the maximum potential for CO_2 removal (E_{pot}):

$$E_{pot} = \frac{tCO_2e}{tOre} = \frac{MW_{CO_2}}{100\%} * \left(\alpha\frac{MgO\%}{MW_{MgO}} + \beta\frac{CaO\%}{MW_{CaO}} + \theta\frac{K_2O\%}{MW_{K_2O}} + \varepsilon\frac{Na_2O\%}{MW_{Na_2O}}\right) * w \qquad (3)$$

Where MW = molecular weight (g mol^{-1}), α, β ε, θ are coefficients which account for redox speciation as a function of pH (1 for pH between 3 and 10; Renforth, 2019) and w = the carbon drawdown per (double-charged) cation flux to the ocean (w=1.5 to 1.7 for typical earth surface environmental conditions (Renforth, 2012, 2019). Hypothetically, if the primary carbon storage pathway is through carbonate mineral formation (carbon mineralization), rather than bicarbonate, then w = 1, reflecting the loss of CDR potential through re-release of CO_2 upon carbonate precipitation.

Most applications of E_{pot} only focus on Ca and Mg, as the contribution of K and Na to the E_{pot} of proposed feedstocks for EW is typically ~25% of that of Ca and Mg (Lewis et al., 2021). Moreover, K (and to a lesser extent Na) are common constituents of chemical fertilizers which may complicate cation budgeting based on field samples. The Steinour equation can also be modified to account for sulfate and phosphate in the rock powder (Renforth, 2019), sourced from salts (e.g., gypsum) pyrite or apatite. In these cases, rock weathering results in cations that are charge balanced by phosphate and sulfate, rather than bicarbonate.

Understanding maximum E_{pot} is important for evaluating various rock powders in order to maximize CDR gains, for initial life cycle assessments (LCA) or first-order global scale models (e.g., Renforth, 2012; Zhang et al., 2022). Even though E_{pot} can be calculated by the cation concentration in the rock, it does not account for the mineralogical composition of the rock powders, where some minerals are more easily dissolved than others, nor does it account for temporal aspects of the reactions. Thus, it is a single, time integrated estimate assuming fully congruent weathering of the feedstock. Its use is also limited by knowledge of the internal variability of the feedstock's chemical composition. Actual CDR from in situ weathering will always be smaller than E_{pot} due to the complexity of mineral weathering and downstream CO_2 losses.

2.2.2 Solid-phase elemental mass balance approach

2.2.2a Principles

The loss of reactants from mineral phases can be used to calculate weathering rates, which may be converted to an initial carbon capture estimate using the E_{pot} of a feedstock. Total soil + rock powder

mobile cation concentrations (e.g. [Ca] & [Mg]) are expected to decrease as mineral dissolution proceeds and mobile cations are lost to solution (Fig. 2). The main advantage of analyzing solid phases in this manner is that it creates a time-integrated signal, whereas other approaches, discussed below, are heavily influenced by climatological and pedogenic parameters leading to more temporally variable signals. Additionally, this approach may be integrated with current agronomic practices as soil samples may be routinely taken by farmers to assess other parameters such as soil pH and cation exchange capacity (CEC). Furthermore, it is possible to constrain weathering signals on a field-by-field basis.

Examining total solids traces the loss of cations in the soil + rock powder to determine weathering rates, but it does not track their export, so converting a rate of cation loss to CDR equivalents will be a maximum estimate of carbon actually exported into the river-ocean system. Additionally, it does not uniquely identify the action of carbonic acid over other potential acids in the soil, which would cause an overestimate of carbon capture at the weathering site.

2.2.2b Immobile tracers for solid phase measurements

A key challenge faced by soil-based cation mass balance is that the contribution of applied rock powder to cation concentrations in the soil and rock powder mixture is not certain, given inhomogeneous application and mixing, sampling constraints, and potential physical erosion or remobilization. This means that cation accounting based on a generalized rock powder application rate for the entire field can result in an over- or under-estimation of the initial cation concentration, even when samples are averaged across a field.

The problem of calculating the initial cation contribution from applied rock powder can be addressed by measuring the concentration of cations in the soil relative to an immobile trace element (such as Ti, Al, Th, Zr) (Reershemius et al., 2023). These principles also underlie the patent of EW operator *Eion Corp.* (Wolf et al., 2023) who, focusing on the rare earth elements (REE) and other immobile tracers, suggest that combinations of immobile tracers can be used to calculate rock powder application rates (see also Kantola et al., 2023). The premise of using immobile tracers in this manner is grounded in traditional sediment geochemistry in that the loss or gain of geochemical components must be expressed relative to a conservative or immobile element that is not involved in the primary reaction (Brimhall and Dietrich, 1987). This creates a normalization procedure that, in this case, accounts for the variable mixtures of rock powder and soil at the sample point, or any erosive loss of rock powders (Fig. 3). In effect, by comparing the concentrations of mobile cations to that of an immobile trace element, a soil + rock powder sample can be pinned along a compositional mixing line between the soil baseline and the rock powder, as shown in Fig. 3. Actual variability in rock powder application

and weathering activity must then be captured by ensuring a high number of samples across the entire site covering representative environmental gradients.

Mass balance approaches using any immobile tracer are predicated on knowing precisely the baseline soil immobile tracer (*i*) and cation (*j*) concentrations, rock powder *i* and *j* concentrations, and the concentrations of *i* and *j* in the mixture after weathering. Essentially, the immobile tracer is used to calculate the amount of cations added to the soil through rock powder spreading, and measurements of post weathering samples of soil + rock powder mixtures inform on the remaining cation amount. The difference in cation concentrations can then be expressed as a fraction of rock powder dissolved (Fd; Fig. 3d) and related back to carbon capture through Eq. 3.

This approach makes two major assumptions. Firstly, the immobile tracer must be demonstrably immobile in the chosen environment. Loss of some immobile tracer from the rock powder will result in a conservative estimate for weathering, but if reprecipitated elsewhere in the soil column may produce a mixed signal for rock powder addition in some samples and therefore distort whole-field weathering estimates. Secondly, cations must be considered fully mobile and generally lost to solution, and will therefore not be present in any solid soil + rock powder sample after weathering. This second assumption, however, is not always applicable as cations can be (sometimes temporarily) incorporated into exchangeable phases or secondary minerals (Amann et al., 2020; Fuhr et al., 2022; Wood et al., 2023). Standard operating procedures for dealing with such exchangeable phases require further development, with some users including pre-leaching treatments to remove them. Sieving of samples to remove larger residual rock fragments and organic debris is usually practiced.

Whilst operationally scalable, one major limitation of using the solid phases for these estimates is the low signal to noise ratios due to high soil cation concentrations. Hence it can be difficult to resolve small differences between the soil–rock mixtures, before and after weathering. To counter this problem, isotope dilution inductively-coupled plasma mass spectrometry (ID-ICP-MS) may be used to improve measurement precision and be better able to resolve small changes in cation concentrations (Reershemius et al., 2023). There may be cases where such high precision is not required, such as where higher rock powder application rates are used, in higher intensity weathering environments, or, generally, when soil and feedstock compositions are very different.

Given the requirement for a precise baseline concentration to be assumed, heterogeneity in soil trace and major element composition represents an appreciable barrier to implementing solid-phase mass balance approaches to tracking weathering at the field scale. This may be at least partly addressed through implementing soil sampling protocols that increase the replicability of measurements (e.g., pooling, geospatial referencing). Statistical treatments of whole-field *i* and *j* concentrations of baseline

and post-application, post-weathering samples will likely be necessary to robustly quantify field-scale compositional changes as a result of EW feedstock application and subsequent dissolution. A key challenge for practitioners will be to assess the minimum sampling requirements for resolvability of these signals in a range of settings, which is currently under-explored in the literature and a recommended priority for ongoing research.

Lastly, the choice of immobile tracer *i* is an important consideration. The concentration of immobile tracer in the rock powder must be significantly higher than in the soil, because: 1) this reduces the requisite analytical precision for measuring a signal for rock powder addition above background noise; and 2) otherwise, at low $\Delta i_{rock\ \ powder\ -\ soil}$, the dissolution of feedstock contributes to a stronger concentration effect of *i,* resulting in a pronounced overestimate of rock powder addition (Reershemius and Suhrhoff, 2023). This effect is true of any element *i*, but can be corrected easily for those elements *i* where concentration in rock powder is several times greater than in soil (Reershemius et al., 2023). Low $\Delta i_{rock\ \ powder\ -\ soil}$ of Th, Nb, Y, and REEs precludes these immobile tracers from being used for most rock powder-soil combinations; this is also true of Ti and Al for most ultramafic rocks, where Cr, Ni and Fe might be the only realistic tracers. Some proposed rock powders for EW, such as wollastonite, do not contain any immobile trace elements in sufficient abundance to be used for this purpose. An additional consideration for an immobile tracer *i* that must be tested thoroughly is the extent of mobility during weathering processes in a range of settings; especially those elements, such as Cr, Ni, Fe, that can also have limited mobility depending on properties such as soil redox state, availability of organic colloids, and pH (Alloway, 2013). Whilst immobility might still be maintained for these elements, heterogeneity in their concentrations vertically and laterally due to diagenetic processes, may lead to biased results.

Kantola et al. (2023) suggest using multiple immobile trace elements in a single calculation to increase the signal strength from rock powder addition in solid phase samples. This involves fitting a regression to the observed concentration increase of multiple immobile trace elements and using the slope of this line to calculate the rock powder application rate (Kantola et al., 2023). However, when using elements that are not particularly enriched in the feedstock, this approach must account for the fact that the concentration increase of multiple immobile trace elements following rock powder addition to a soil is also a function of the relative concentration differences between rock powder and soil for each individual element, and will be affected by feedstock dissolution (Reershemius and Suhrhoff, 2023). Moreover, analytical uncertainties must be appropriately propagated to ensure accuracy and significance of interpretations based on regression models. A different approach to increasing the strength of a signal for rock powder addition may instead be to pin to a ratio of immobile tracers, where the denominator is a tracer that is less concentrated in the rock powder than in the soil (e.g. Th).

It is clear that more work is needed to develop methods to refine soil-based mass balance for estimating in-field weathering rates of rock powder: primarily to improve sampling and analytical practices while limiting their cost, to resolve spatial variability in estimates of field-scale weathering rates, and to take into account processes such as fertilizer addition and background weathering of soil constituents that may interfere with signals. Moreover, assumptions on tracer (im)mobility require testing in more local environments before such methods can be robustly used for widespread CDR crediting purposes.

2.2.3 Accumulation of soil inorganic carbon

With some reactive feedstocks (e.g., slag and wollastonite) or under certain climatic conditions (low rainfall, high soil pH) carbonate precipitation may be favored over aqueous bicarbonate creation, termed carbonation or CO_2 mineralization (Campbell et al., 2022). The CDR efficiency of the mineralization pathway is half that of EW with bicarbonate formation due to CO_2 release during carbonation (Fig. 2). In these cases, the formation of carbonate can be monitored as total inorganic carbon (TIC). At high enough concentrations, TIC is relatively simple to quantify using calcimetry or thermogravimetric analysis and, if enough carbonate is generated, can be combined with techniques such as XRD analysis to characterize the carbonate mineralogy (Dudhaiya et al., 2019; Haque et al., 2019, 2020, 2023; Khalidy et al., 2021). Additionally, the source of carbon and calcium can be quantified using isotopic tracers (see Section 2.5; radiogenic Sr isotopes to confirm the source of Ca, and stable carbon and oxygen isotopes to confirm the source of carbon) to ensure the accumulation of TIC came from mineralization of silicate minerals (Knapp et al., 2023).

2.3 Accumulation of weathering products in exchangeable phases

Dietzen and Rosing (2023) suggest monitoring cation accumulation in exchangeable phases as a pathway to carbon capture estimates, which may potentially be easier to resolve compared to total solids approaches. In principle, this approach is based on the opposite assumption compared to solid phase approaches: namely that all released mobile cations are not leaving the top soil but are retained on exchangeable sites for the period in question. Exchangeable phases are geochemically reactive components (clays, oxides and organic matter) within a soil that have the capacity to weakly bind cations to their negatively charged surfaces. These reactions are typically considered to be rapid, operating on the order of seconds to days and may include sorption and surface precipitation (Brady and Weil, 2008). Often the exchangeable phases include elements bound to clays and oxides minerals, but not the elements incorporated into these minerals on longer timescales due to diagenetic stabilization. Elements weakly bound to organic matter can also be included, but not those directly

incorporated into more recalcitrant organic substances (Brady and Weil, 2008). Note that some literature sources refer to 'bioavailable', 'reactive' or 'labile' pools to distinguish phases that are separate to non-reactive, inert mineral phases (Bhatia et al., 2013; Larkin et al., 2021). There will be overlap between such phases and the exchangeable pool, however, in reality, all of these terminologies are operationally defined based on leaching protocols and are rarely exclusive in their extraction (Brown, 1943; Tessier et al., 1979; Groenenberg et al., 2017; Vienne et al., 2022; Vink et al., 2022; Dietzen and Rosing, 2023).

The precision of this method therefore relies on correctly timing soil sampling, and any loss of cations from top soils to ground water will not be detected. Given that water (and hence the flushing of cations from top soils) is a necessary condition for weathering to occur, the validity of these assumptions and the temporal decoupling of weathering and cation transport can be questioned. Dietzen and Rosing (2023) suggest that baseline monitoring of exchangeable and fluid phases could be used to identify time periods where the loss of cations to fluids is minimal, allowing measurements from the exchangeable fraction from particular seasonal points to be used for CDR estimates. But, there will always be a risk of underestimating cation losses.

In some EW experiments, there is no evidence for significant cation removal by exchangeable phases (Renforth et al., 2015), whilst others demonstrate quantitatively important interactions between cations and secondary minerals, such as clays (Pogge von Strandmann et al., 2019, 2021; Dietzen and Rosing, 2023), even up to a 100 x the concentrations seen in leachate data (Kelland et al., 2020). Given the potential control of exchangeable pools onto the weathering mass balance, they may be a limiting factor for identifying weathering products from solution based methods, and a suggested contributor for the lack of observed weathering signals in outflow waters of field trials, particularly in low pH soils (Larkin et al., 2022). Such behavior will depend on the base saturation state of the exchange sites as well as soil permeability, pH, net cation exchange capacity (CEC) and surplus rainfall. If there is a low CEC or high pH, base saturated soil, it will be more likely that cations are transported out of the soil.

2.4 Aqueous phases

2.4.1 Overview

With a similar logic to examining exchangeable phases, accumulation of weathering products in aqueous phases can also produce a wealth of information on cations and anions, including carbon species (Renforth et al., 2015; Shao et al., 2015; Vienne et al., 2022; te Pas et al., 2023). In experimental setups, such as columns, pots and mesocosms, the aqueous phase is often collected as a

‘leachate’; that is a fluid that has penetrated the soil, mobilized weathering products and exited the experimental setup into a collector. Infield sampling may be done via the collection of pore waters through Macro Rhizon syringes, via soil lysimeters (e.g., suction cup or tension lysimeters) or even shallow wells at specific depths in the soil column (see Almaraz et al., 2022). Artificial cation-exchange resins in the soil have also been suggested as a method to sample waters by the patent of Wolf et al., (2023) but to date, there is no published research validating this approach. Anion exchange resins have also been used to measure nitrate and ammonia (Kantola et al., 2023).

Catchment or watershed scale monitoring on rivers or channels have been applied to larger scales of deployment, providing integrated total system fluxes (Andrews and Taylor, 2019; Larkin et al., 2022; Knapp et al., 2023). Indeed, monitoring of dissolved loads at the riverine catchment scale is the primary method by which current global CO_2 removal via natural weathering is measured (Gaillardet et al., 1999b; Viers et al., 2007; Hartmann et al., 2014; Moon et al., 2014; Hilton and West, 2020) hinting at the scalability of this approach. It may also be possible to monitor drainage waters via carefully designed artificial drainage systems (e.g., tile drains) to capture water exiting a site (Andrews and Taylor, 2019).

In the field, the location, depth and timing of solution sampling will have implications for how measurements will be related back to carbon capture estimates. For pore-water samples, data will likely primarily reflect reactions at the weathering site including primary dissolution and secondary uptake of weathering products. Water moving through a soil may be subject to additional geochemical processing, such as adhesion to cation exchange sites (Pogge von Strandmann et al., 2019), that could modify the EW signal. By contrast, measurements made at the catchment scale can provide total system fluxes, averaging out small scale heterogeneities.

For all solution-based analysis in the field environment, challenges exist in the temporal signature of aqueous phases that can vary seasonally, for example with rainfall amount and intensity that affect dissolution kinetics, dilution, water flow paths through the soil, transit times and total cation export (Calabrese et al., 2017; Wen et al., 2022), requiring detailed temporal consideration on sampling strategies (Dietzen and Rosing, 2023) and how measurements are scaled to annual CDR estimates. Additionally, particularly at large scales, it might take years for a resolvable trend to emerge (Taylor et al., 2021) and so long-term monitoring, large-scale and carefully designed experiments might be required, in combination with scientific guidance on sampling intervals for robust CDR estimates.

Solution based analysis requires assessment of water flow in order to convert concentrations into a flux (the total amount of inorganic carbon exiting to catchment waters per year) and ultimately calculate the mass of carbon exiting the system. Typically there is a measurement resolution mismatch

between how often a discharge measurement is taken or modeled (resolution of minutes to daily) and how often a concentration measurement is made (at least biweekly, sometimes monthly). Therefore, a load estimation method is required to calculate an annual flux (e.g. Moatar and Meybeck, 2005). Chosen load estimation methods require some assumptions to be made about concentration behavior in between sampling points. Measurement of discharge at the watershed scale may be more straightforward with the proper installation and calibration of a gauging station. At the smaller field scale, modeling or calculation of predicted flow based on measured climatic parameters (via an onsite weather station) and physical soil properties can be used to estimate discharge (Alley, 1984; McCabe and Markstrom, 2007).

2.4.2 Base cations and dissolved silicon

The base cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) are mobile, and form the main dissolved cations in natural waters. Potassium (K^{+}) and (Ca^{2+}) are more likely to be uptaken by plants, with potassium being a key nutrient. Sodium (Na^{+}) and potassium (K^{+}), are more likely to remain in the aqueous phase, but are limited by their availability in CDR rock powders and have a lower CDR potential per mass due to forming singly charged cations. Ca^{2+} and Mg^{2+} are more abundant in CDR rock powders but are more likely to adhere to the exchangeable sites (Whitworth, 1998; Bergaya et al., 2006; Dietzen and Rosing, 2023), and Ca^{2+} will form pedogenic carbonates in some EW operations (Haque et al., 2020; Khalidy et al., 2021). Numerous studies suggest that Mg^{2+} is the most suitable cation for estimating weathering rates in the exchangeable fraction and plays a larger role in potential CO_2 uptake (Renforth et al., 2015; Pogge von Strandmann et al., 2021; Dietzen and Rosing, 2023). Moreover, given that Mg^{2+} is not as readily incorporated into carbonate minerals or uptaken by plants compared to Ca^{2+}, it may be easier to trace in solutions.

Similarly, Si will be a major component of many EW feedstocks and its presence in solution could directly indicate weathering activity. It is more difficult, however, to relate Si concentrations back to carbon capture given the mineral partitioning of Si within the feedstock. For example, the presence of Si in non-alkaline silicate minerals (including amorphous phases) could supply Si without cations. Silicon can also be removed from solution to form secondary minerals (e.g. Kelland et al., 2020). It has furthermore been suggested that silica saturation may limit feedstock dissolution and the CDR potential of EW (Köhler et al., 2010; Hartmann et al., 2013; Harrington et al., 2023), however the role of silica saturation in limiting enhanced weathering is debated (Schuiling et al., 2011).

2.4.3 Anions

In natural waters at neutral range pH, the dominant dissolved anions are sulfate, nitrate, chloride and bicarbonate. Minor contributions from phosphate and borate may be present in some waters. The sum of major anions (Cl^-, SO_4^{2-}, NO_3^- HCO_3^-) minus the sum of major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) in equivalents is equal to zero due to the law of electroneutrality. The normalized inorganic charge balance (NCIB = $(\Sigma+ - \Sigma-)/(\Sigma+ + \Sigma-)$ in %, where $\Sigma+$ is the sum of cations and $\Sigma-$ is the sum of anions, in equivalents) or charge balance error (CBE) is a key indicator of water data quality, with values typically greater than ±5% for high quality measurements, and should always be within ±10% (Fritz, 1994).

Measurement of anions are required to understand not only the quality of the measurement but also to understand the acidity source (carbonic acid vs. strong acids; see section 3.2), and to correct cation measurements for rainwater inputs (cyclic salts) and dissolution of evaporites (such as gypsum that is commonly used as an agricultural amendment). Bicarbonate concentrations in neutral range pH waters may be calculated using major anion and cation measurements via charge balance, assuming that all remaining positive charge after subtracting Cl^-, SO_4^{2-}, NO_3^- (in equivalents) is charge balanced by HCO_3^- (e.g., Galy and France-Lanord, 1999).

2.4.4 Total alkalinity (TA), pH and DIC

Dissolved inorganic carbon (DIC) is a term used to encompass all inorganic carbon species in a liquid, including CO_2, carbonate, bicarbonate and carbonic acid. Thus, it can give the most direct measurement of bicarbonate release from mineral weathering (Amann et al., 2020; Almaraz et al., 2022). DIC measurements can be performed with several types of equipment that require minimal technical skills (e.g., coulometry). For soil pore waters, the main issue is that the partial pressure of CO_2 (pCO_2) is much higher than atmospheric pCO_2 due to respiration. Thus, samples need to be hermetically saved (and with minimum headspace), from the moment they are collected in the field until they are analyzed, to avoid degassing of molecular CO_2 (Reiman and Xu, 2019). Special care needs to be taken for samples at lower pH values in which the concentration of dissolved molecular CO_2 is higher. In other cases, samples can be left open to the air to equilibrate with atmospheric CO_2, after which DIC can be measured a second time, simulating equilibration which would have happened when the soil pore-waters enter a watershed.

In neutral pH waters, DIC can be approximated by total alkalinity (TA) measurements. This is only true, however, if the only proton (H^+) receptors (the bases) are largely from hydroxide (OH^-), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), and pH is between 6.3 and 10.3 (see Bjerrum plot, Fig. 5). More strictly, TA refers to the milliequivalents (mEq) of H^+ used while titrating a water sample with

an acid of known concentration, usually via Gran Titration (Gran, 1952; Stumm and Morgan, 1996; Wolf-Gladrow et al., 2007). Thus, the measured TA is an approximation for DIC, which in most natural freshwaters is bicarbonate, and hence can be used to estimate CDR. Any two of alkalinity, pH, pCO_2 and DIC can be used to calculate bicarbonate concentrations in waters. These calculations can be performed in PHREEQC (Parkhurst, 1995).

The advantage of TA is that it is a simple measurement to make with no specialist equipment needed, and is routinely measured during watershed monitoring by, for example, governmental bodies (Hartmann et al., 2014; USGS, 2019). Total alkalinity is a conventional parameter used to calculate the bicarbonate concentration of natural freshwaters at circum-neutral pH (Andrews et al., 2016; Amann and Hartmann, 2022; Holzer et al., 2023a; Knapp et al., 2023). Caution should be maintained, however, as TA can be affected by the presence of other accepting bases in addition to DIC. For example, in waters with high dissolved organic carbon (DOC), total alkalinity might be a poor approximation for bicarbonate concentrations (Wolf-Gladrow et al., 2007; Kerr et al., 2021).

2.4.5 Electrical conductivity (EC)

Electrical conductivity (EC) reflects the total ion concentration of a solution and hence can proxy the accumulation of weathering products, offering a potentially more scalable solution to CDR monitoring. The benefit is that EC can potentially be monitored in real time using sensors, whilst TA requires ex-situ lab analysis. Amman & Hartmann (2022) identified consistent correlations between TA and EC, thought to reflect the covariation of TA and cation concentrations. This potentially means EC could be used in specific situations, coupled with pH measurements, where assumptions about TA and DIC speciation can be made and bicarbonate concentrations can be calculated successfully using speciation modeling software such as PHREEQC (Parkhurst, 1995). Robust and representative calibration datasets should be used to validate and monitor the use of EC in field environments as the relationship of EC to TA will vary with different ionic compositions.

2.5 Isotopes

2.5.1 Overview

Measuring isotope compositions is more expensive than most of the MRV approaches introduced thus far, and requires more specialist infrastructure, thus they are less likely to be an integral part of routine MRV approaches. However, isotope-based approaches can yield additional important information that is complementary to other methods and provide a fuller picture of the EW process. In particular, they

can play a fundamental role in determining some of the underlying processes and in calibrating reactive transport models.

The approaches in the previous sections all have in common that they assess the absolute concentrations of certain elements or ions. While it is essential to assess elemental reservoirs and fluxes, isotope ratios can yield additional information such as the nature of the sources and sinks of elemental fluxes, or processes that modulate these fluxes (Faure and Mensing, 2005). For example, stable isotope systems are often used to infer mixing of different element sources, as different sources can have very different isotope signatures. They are also used to infer processes such as the formation of secondary phases or cation sorption onto exchangeable sites because some isotopes are easier to exchange, for example as a result of higher or lower mass (i.e., they fractionate them).

Radiogenic isotope systems are typically used to trace sources rather than processes. As a result, for traditional radiogenic isotope ratios, sample composition typically depends on the isotope composition of the source mineralogical phases. Complexity in interpretation arises, however, because isotope ratios are usually modified by secondary controls, such as biological (e.g. respiration), environmental (e.g. temperature) or procedural (e.g. laboratory separation and measurement) processes.

2.5.2 Stable carbon and oxygen isotopes

Stable carbon and oxygen isotopes ($\delta^{13}C$ and $\delta^{18}O$) are relatively simple to measure and can inform on the source of C in soil fluids and carbonates. If the $\delta^{13}C$ of each carbon source is distinct and known, then measured $\delta^{13}C$ of water outflows could inform on the relative proportion of each source (Manning et al., 2013). For example, CO_2 in soil waters is typically derived from organic respiration, giving it a low $\delta^{13}C$ value (-27 to -12.5‰; Vogel, 1993), whereas carbonate rocks and carbonate amendments ('AgLime'), derived from marine carbonate deposits, have higher, and distinct, $\delta^{13}C$ values. Potentially $\delta^{13}C$, coupled with $\delta^{18}O$, can help separate sources of C and identify contributions from silicate weathering vs. carbonate weathering in fluids as well as pedogenic and lithogenic carbonates in soils (Cerling, 1984; Schulte et al., 2011). To date, $\delta^{13}C$ and $\delta^{18}O$ have been used to partition sources in carbonates at enhanced weathering sites (Knapp et al., 2023).

2.5.3 Radiocarbon

Radiocarbon (^{14}C-dating) is expensive to analyze and requires both specialist preparation of samples, and equipment for measurement (e.g., accelerator mass spectrometry). However, radiocarbon can provide valuable insights into the age of products derived from enhanced weathering, and can help to pin-point modern atmospheric carbon sources with lower uncertainty than traditional stable carbon and oxygen isotopes (Knapp et al., 2023). Radiocarbon may be incorporated into the products of

enhanced weathering, such as carbonates, derived from atmospheric CO_2 which currently has a fixed ^{14}C content from cosmic production in the atmosphere. Once incorporated, ^{14}C starts to decay and the age of the carbonate since formation can be measured. Older sources of carbon (>~60 kyrs), such as bedrock carbonate and shales, have isotopically 'dead' C, where ^{14}C has fully decayed, potentially helping separate carbon supplied by EW from other sources of C in the system. Coupled with total carbon content, it is possible to extract a rate of atmospheric C removal using this technique (Knapp et al., 2023). Nevertheless, caution should be exercised when using both radiocarbon and stable carbon isotopes as these methods are affected by CO_2 exchange and kinetic fractionation that may lead to misleading interpretations (Stubbs et al., 2023).

2.5.4 Radiogenic strontium

Radiogenic strontium (Sr) isotopes ($^{87}Sr/^{86}Sr$) are a common tracer for natural weathering reactions and sources of weathering fluxes (Blum and Erel, 2003; Faure and Mensing, 2005). Radiogenic Sr (^{87}Sr) is produced from ^{87}Rb through radioactive (β-) decay; hence the name radiogenic. Radiogenic Sr is usually normalized to non-radiogenic, stable ^{86}Sr to facilitate comparison between phases with different Sr concentrations (Blum, 1995; Blum & Erel, 1995, 2003). Silicate rock $^{87}Sr/^{86}Sr$ differ according to rock type (mantle or crustal, as Rb and Sr are fractionated during partial melting, with Rb concentrated in the melt) and age (Blum and Erel, 2003; Faure and Mensing, 2005). Carbonates and evaporites can inherit $^{87}Sr/^{86}Sr$ values from the ocean in which they are deposited, and have values which are distinct, and typically lower, than silicates. As a result, different rock types have distinct isotope compositions that can be used to trace the dissolution of silicate feedstocks in EW.

Strontium cations are relatively mobile, and Sr readily substitutes for Ca in minerals as they have similar atomic radii. Strontium enters pore waters and streams on a similar timescale as major cations, and therefore can be used to trace cation sources, in particular Ca. Hence, the isotope composition of Sr in effluent water can be used to investigate what mineralogical phases contribute to the dissolved signals through their dissolution (Larkin et al., 2022). If the Sr isotope composition of soils and feedstocks, as well as Sr concentrations of the feedstock, are known, this can be used to estimate lithology-specific weathering rates at catchment scales (Négrel et al., 1993; Gaillardet et al., 1999a; Suhrhoff et al., 2022). This approach has also been applied to EW and used to estimate the relative cation flux contribution of carbonate and silicate weathering, and hence calculate CDR using cation stoichiometry (Larkin et al., 2022). Caution should be applied when using radiogenic Sr if EW feedstocks contain carbonates, as carbonates dissolve much quicker than silicate minerals and even trace amounts of carbonates are sufficient to dominate Sr isotope signatures of weathering fluxes, particularly in early weathering stages (Harris et al., 1998; Aubert et al., 2001; Jacobson et al., 2002).

2.5.5 Novel isotope tracers

Novel isotope tracers, such as magnesium (Mg), lithium (Li), silicon (Si), and stable strontium (Sr) can be used to trace processes such as secondary mineral formation. The majority of work to date on these isotope systems has revolved around quantifying fractionation factors and natural element cycling (Penniston-Dorland et al., 2017; Teng et al., 2017), but EW-specific applications are increasing (Pogge von Strandmann et al., 2021; Vienne et al., 2023). For these isotopic tracers strong fractionations are induced by interactions with secondary minerals, thus potentially allowing quantification of secondary mineral formation using isotope mass balance, that could inform on cation loss to exchangeable phases, or potential re-release of CO_2 during secondary mineral formation (see section 3.3; Campbell et al., 2022). The initial isotope signature of different feedstocks might also be sufficiently unique to use as a source tracing tool, similar to radiogenic Sr.

2.6 Gaseous phase

Less research is available on the use of gas phase measurement for tracing EW in agricultural settings, which has been demonstrated in mine waste EW applications (e.g., Stubbs et al., 2022). However, in principle, changes in soil pCO_2 and soil CO_2 efflux could be used to calculate CDR. Carbon dioxide removal by EW could potentially lead to a measurable decrease in the CO_2 efflux at the soil surface. Resolution of the EW signal is, however, unlikely in most cases as CO_2 fluxes from organic cycling tend to be an order of magnitude higher than inorganic (Weil and Brady, 2017). Gas measurements could further be expanded to include other GHG fluxes like CH_4 and N_2O, which can also be influenced by rock powder application (Chiaravalloti et al., 2023).

Varying interpretations about the effects of rock powders on gas fluxes have been obtained to date using gas flux chambers. Dietzen et al. (2018) found no significant increase for cumulative CO_2 emissions for high rates of olivine application in an incubation experiment with organic rich acidic topsoil (0-10 cm), although corresponding lime application increased CO_2 by 221%. In a similar experiment, Yan et al. (2023) found significantly increased CO_2 emissions due to soil organic carbon mineralization when mixing 12 different soil types with wollastonite (although wollastonite application is extremely high at 10 wt%). Vienne et al. (2023) found significantly reduced CO_2 emissions in a mesocosm experiment with high (100 t ha^{-1}) basalt application rates compared to their control, although the addition of earthworms to the basalt plots increased the emission. Preliminary results of automated CO_2 measurements point towards more significant and consistent data than for all other phases (plant, soil, water), but identify an overall increase in CO_2 efflux from soils (Paessler et al., 2023). Gas measurements with the flux chamber LI-COR system confirm the CO_2 drawdown potential of ultramafic rocks and oxides (Rausis et al., 2022; Stubbs et al., 2022), although these experiments were conducted without soil.

Despite being important contributions to the nascent field of gas phase measurements, a major limitation of the flux chamber approach (Vienne et al., 2023) is that those are point measurements of the highly variable daily CO_2 flux curve. The extrapolations of these point measurements might result in significantly different results depending on the spatio-temporal pattern with which measurements have been taken. Automated flux chamber experiments (Paessler et al., 2023) can partly overcome the temporal resolution problem but are not a scalable solution. Besides the importance of feedstock mineralogy, these studies found the major parameters influencing CO_2 drawdown efficiency to be water content, porosity, and permeability. Large scale measurements have been employed through eddy covariance towers (Kantola et al., 2023). These measurement towers yield valuable data about overall ecosystem carbon dynamics. However, the sensor height of somewhere between 1 to 2.5 m might cause significant dilution of the gas phase through the overlay of various fluxes, and thus not provide the necessary resolution needed for in-depth discrimination of driving mechanisms.

3 Sources of uncertainties in CDR estimates

3.1 Multidimensionality and sampling strategies

A comprehensive measurement strategy will capture variability in CDR estimates incorporating natural infield spatial and temporal variability, systematic uncertainty from measurement approaches, and analytical external reproducibility. We expect a multidimensional approach would create a pool of CDR estimates and would allow for a data distribution to be generated. Such an intercomparison would also allow for internal consistency checks and quality control on all data generated, including identification and investigation of any outliers. The most conservative estimate of CDR would be to utilize the lowermost capture estimates, as this corresponds to a high probability of removal. However, combining different measurement methods and spatial scales would allow for statistical treatment of all datasets and a distribution to be produced, resulting in an overall CDR estimate with appropriate confidence intervals. Uncertainty could then translate into carbon removal credit discounting, similar to suggestions from *Frontier* based on Verification Confidence Levels (Klitzke et al., 2022). Understanding any systematic biases and assumptions, due to different measurement approaches, will be paramount to produce the most accurate and precise CDR value. In addition to this, measurement and accurate quantification of the baseline and counterfactual scenario, which will need to be dynamic and measured via suitable controlled trials, has to be taken into consideration in the overall measurement. Understanding and appropriate consideration of statistical significance, heterogeneity and error propagation are central to proper interpretation of any data generated. Compounded with uncertainties from measurement approaches, all methods are limited by the ability

to produce data that is representative of the EW activity area. Currently, there is no guidance from standard bodies for how to handle representative sampling specific to EW (Campbell et al., 2023).

Additional uncertainties may derive from the estimates of rock powder application rate. The logistically simplest method to estimate application rates is via spreading operation data. Alternatively, there is potential for using immobile trace elements in pre- and post- application soils to either estimate true applications rates, or use as a normalization procedure to account for application rate variance (Kantola et al., 2023; Reershemius et al., 2023; Wolf et al., 2023). These solid phase approaches, however, rely on accurate extrapolation across a deployment area. Importantly, high application rates (50–100 t ha^{-1}) that exceed practical agronomic application rates (1–20 t /ha^{-1}, Swoboda et al., 2022) are typical for most ongoing EW experiments in order to obtain clear signals. However, such large amounts, especially when surface applied or mixed only in a shallow (0–10 cm) soil layer, might introduce alkalinity hotspots upon dissolution and thereby significantly alter the micro- and macropore saturation states, which could in turn slow dissolution kinetics. Thus, extrapolating CO_2 drawdown rates from such high application amounts might be prone to error.

Temporal uncertainty is perhaps one of the largest limiting factors for EW measurement approaches. The weathering of silicate minerals is a continuum, meaning that the removal of CO_2 on site follows a weathering curve which may continue on decadal to centennial timescales (Kanzaki et al., 2022). Each method outlined here is applicable to certain time windows, with only solid phase measurements providing a temporally integrated weathering measure. In addition to this, there is spatial and temporal overlap between mineral dissolution, transport and storage (Fig. 1). While beyond the scope of this review, we call for clear guidance from regulators as to what point in time a credit can be issued relative to measurement taken at the weathering site.

3.2 Non-carbonic acids

The long term use of chemical, nitrogen and phosphorus based fertilizers in nutrient poor soils may lead to complications for tracing enhanced weathering as well as reducing the CDR efficiency (Andrews and Taylor, 2019). Application of certain fertilizers may lead to the formation of strong mineral acids, including nitric and phosphoric acid. Sulfuric acid can also be present if feedstocks, such as some ultramafic rock types, contain sulfide minerals (Lerman and Wu, 2006; Horan et al., 2019; Relph et al., 2021). Non-carbonic acids present multiple complications for CDR estimates (Taylor et al., 2021; Zhang et al., 2022). Firstly, they are much stronger than carbonic acids, and hence readily provide acidity for mineral dissolution. This means that alkaline silicate minerals can be dissolved by non-carbonic acids, releasing cations (red-dashed arrow, Fig. 2), but with no CO_2 sequestration (no HCO_3^- formation), effectively decreasing the CDR potential for the rock powder.

That said, the export of cations from the weathering site could help buffer downstream processes and CO_2 loss.

As a result of unknown acid dissolutions, any CDR method that measures only cation concentrations as a weathering product (such as soil only approaches) cannot distinguish which acid caused weathering and hence the true amount of CO_2 removed. For liquid based approaches, however, it may be possible to use the relationship of HCO_3^- vs. [Ca^{2+} + Mg^{2+}] as evidence for carbonic acid weathering (after correcting for rainfall and fertilizer salts; Hamilton et al., 2007; Perrin et al., 2008; Larkin et al., 2022). Non-carbonic acid weathering supplies cations without HCO_3^-, creating anomalous bicarbonate-cation relationships. Furthermore, water NO_3^- concentrations could be used to estimate the degree of onsite/in situ strong acid weathering and correct for cation supply by strong acids, helping refine CDR estimates in the case of fertilizer use (Larkin et al., 2022). A recent study on EW with basalt powders in the midwest USA identified that less than 2% of the total cation flux was derived from nitric acids (Kantola et al., 2023), hinting that such losses may be minor. But this must be characterized for more environments. Moreover, nitrate, as a key nutrient, is short-lived in most natural environments (Meybeck, 1982) and so the long term fate of weathering products from nitric acid weathering is not known. Dietzen and Rosing (2023) suggest that the contribution of non-carbonic acids to soil pH can be accounted for using the difference between pH predicted by pCO_2 alone and the true pH of the soil, potentially deriving a correction factor for mineral weathering due to non-carbonic acids. Importantly, their approach suggests that, depending on soil pCO_2, below pH 4.5-5.5, more than 50% of weathering occurs due to strong acids. Only above a pH of 5.2-6 (again, depending on soil pCO_2) can most of the weathering be assumed to derive from carbonic acid. Clearly, in such settings, accurate quantification of strong acid weathering is of prime importance for overall carbon budgets.

Even if estimates of non-carbonic acid weathering can be made, high baseline weathering rates, caused by extensive historical fertilizer use, can decrease the signal–baseline ratio making it difficult to resolve weathering changes as a result of EW activity (Larkin et al., 2022). Cation interactions with fertilizer components can add further complications to measuring protocols, for example the formation of hydroxyapatite minerals (Wood et al., 2023) that remove cations from solution but are robust enough to avoid extraction via leaching methods.

Similar to the ongoing literature discussions of Ag-lime as a source or sink of CO_2, in the case where soil (pedogenic) carbonates are a significant storage pool, strong acids present a risk of reversal (storage failure) through carbonate dissolution. CO_2 emission is also applicable if the EW material itself contains any carbonate minerals, e.g., in concrete, or trace calcite in mafic rocks (Dietzen et al., 2018; Kemp et al., 2022; Larkin et al., 2022; Zhang et al., 2022). Ag-lime, as well as silicate minerals,

may also potentially help offset excess acidity from non-carbonic acids, allowing further weathering by carbonate or silicate minerals to be via carbonic acid instead (Hamilton et al., 2007).

3.3 Authigenic clay formation

With the supply of silica, aluminum, iron and cations from rock powder dissolution, the formation of secondary minerals is naturally enhanced. In addition to carbonate minerals, the most common secondary minerals are authigenic clays, amorphous silica, metal oxides and oxyhydroxides. Their formation is a function of weathering congruence, a term that describes the tendency for a mineral to dissolve completely and for the weathering products to be removed in solution, and is controlled by factors such as dissolution kinetics, ambient conditions (pH, eH), rainfall and especially porosity and permeability. Secondary minerals can form coatings on primary minerals, thereby isolating the mineral surface from reactive fluids and decreasing weathering rates, but the impact on dissolution rates is highly contextual (see Oelkers et al., 2019 for review).

By extension, it is not clear if CDR and its rate linearly increase with feedstock application, or whether high feedstock application rates promote supersaturation of secondary phases and surface passivation, which may act as a negative feedback on the CDR rate. Potentially, secondary mineral formation could increase reaction kinetics in some cases as high elemental saturation states may limit primary mineral dissolution (Köhler et al., 2010; Schuiling et al., 2011). Secondary precipitates can thereby decrease the fluid saturation state and potentially promote primary mineral dissolution (Harrington et al., 2023). From a monitoring perspective, secondary minerals increase the cation exchange capacity of the soil, which has implications for identifying weathering signals using liquids.

One further complication deriving from authigenic clay mineral formation ("reverse weathering") is the potential for CO_2 degassing (Fuhr et al., 2022) e.g.:

$$0.15Ca^{2+} + 0.1Na^{+} + 2.5Mg^{2+} + 0.1Fe^{2+} + 7HCO_3^{-} + 3H_4SiO_4 + Al(OH)_3 \rightarrow Ca_{0.15}Na_{0.1}Mg_{2.5}Fe_{0.8}Si_3AlO_{10}(OH)_2 + 7CO_2 + 10H_2O \quad (3)$$

In marine settings, the importance of reverse weathering, and increased CO_2 flux, is clear for global carbon cycling on geological time scales (Isson and Planavsky, 2018; Bayon et al., 2022). That said, the role of reserve weathering in terrestrial soils and EW applications is poorly understood (Renforth and Campbell, 2021).

3.4 Vegetation

Vegetation represents an immediate complication for CDR estimates based on liquids and exchangeable phase analysis, as they will selectively remove weathering products from solution. Thus, in order to complete the weathering mass balance, vegetation must be sampled to estimate cation loss from the system (Shao et al., 2015; Reershemius et al., 2023). Without accounting for this cation loss, there is a risk of underestimating the cation released by rock powder dissolution. That said, the effects are dependant on the cation species, and plant uptake has been shown to be relatively minor in comparison to cation release from basalt powder by weathering in EW field trials with corn/soy and miscanthus in the US Midwest (Kantola et al., 2023). Monitoring vegetation chemistry is also important for understanding the health risk of metals sourced from rock powders (Dupla et al., 2023), and must follow standardized agronomy practices that consider metal compartmentalization in plants and decrease exposure risk (Brune et al., 1995; Thomas and Reid, 2021). One of the biggest limitations caused by vegetation is simply the removal of liquids from the soil, which makes in-field liquids sampling difficult and contributes to uncertainty in flow rate calculations.

The impacts of cation removal by vegetation on wider system carbon cycling is currently understudied. For example, the vegetative removal of cations will disturb the charge balance of anions, including bicarbonate, in remaining pore waters (Britto and Kronzucker, 2008; Amann et al., 2022). The spatial and temporal aspects must also be considered, as, similar to organic carbon cycling, cation cycling in vegetation will be short term with the potential to return cations to the weathering system (Banwart et al., 2009).

4 Discussion and Conclusion

While EW is a relatively new approach to CDR, the underlying science behind quantifying weathering rates in soils is well established and EW specific research is progressing rapidly. Moreover, while quantification of both weathering and subsequent carbonation rates should be advanced further through research, multiple methods exist today that are readily available to form the foundation of MRV approaches, primarily through tracking mineral constituents or directly monitoring bicarbonate formation and export. The majority of measurement types can be made in different settings, including experiments that explore weathering fundamentals and dissolution kinetics, or field settings that monitor real world processes. This allows for a detailed determination of weathering parameters through the combination of several measurement types, and a more robust estimate of atmospheric CO_2 removal. The efficacy of each approach in EW operations will vary with application material, soil conditions and soil management strategies that dictate the level of complexity of the system.

Considering the future scaling of the EW industry to reach the projected gigatonne removal potential, robust measurement campaigns can provide the foundation for geochemical modeling, including EW specific reactive transport models (Kelland et al., 2020; Kanzaki et al., 2022; Vienne et al., 2022). However, a strong measurement component is urgently required to refine, calibrate and validate geochemical models. This is particularly relevant as current favored reaction transport or simplified dissolution models are described as more comparable to closed system batch reactors than natural field conditions, lacking real world processes such as wetting-drying cycles, spatial resolution of permeability and flow paths, secondary mineral formation (Kelland et al., 2020) or exchange processes (Beerling et al., 2020; Kantzas et al., 2022). Moreover, there is large uncertainty in core input parameters such as mineral dissolution kinetics (Calabrese et al., 2022) and models calibrated under certain experimental setups fail to predict empirical datasets in other applications (Vienne et al., 2022). The EW community would benefit from an intermodel comparison project, similar to those used for climate models (CMIP), especially when considering downstream processes.

The success of EW as a CDR pathway will vary based on localized factors (e.g., climatic, geologic and agricultural; Cipolla et al., 2021, 2022), analogous to controls on natural weathering rates (West et al., 2005; Brantley et al., 2023), as well as rock type (mineralogy, particle size and surface area; Taylor et al., 2016; Renforth, 2019). Whilst rock powder dissolution in soil environments is highly complex at a local scale, leading to high spatial variability in measurements, this variability will become averaged out at larger spatial scales. As EW operations in a given catchment area expand, riverine monitoring may become the primary approach for quantification of carbon removed, rendering measurements at the soil level of secondary importance. To successfully identify enhanced weathering signals in rivers, however, requires that the signal is resolvable over baseline variability, which is challenging in environments of high baseline weathering activity, for example due to historic fertilizer use (Larkin et al., 2022; Mu et al., 2023). Innovative approaches to monitoring over larger spatial and temporal scales should be explored, as they may be required to complement local measurements and models for deployment at scales of megatonne or gigatonne CDR across wider geographies.

All measurement approaches require an accurate dynamic baseline via controlled trials (e.g., ‘untreated’ measurements) to quantify counterfactual weathering rates, that is, carbon capture that would have happened in the absence of application of EW feedstocks. This is particularly important to understand if feedstocks are replacing other agricultural amendments (such as Ag-lime or synthetic fertilizers) or in scenarios where rock powder application might already be practiced (albeit at lower application rates than are typical for EW; Swoboda et al., 2022). It is important that the baseline operations cover highly comparable geographic and climatic gradients as active EW applications.

At this point in time, all EW operations, private sector or academic, are in a phase where data production is paramount to collectively solve the challenges of quantifying weathering activity. Given the complexity of the soil system, and potential for competing processes to create uncertainty, we stress that multidimensional measurement campaigns should be undertaken and prioritized. Ultimately, scaling of EW will depend on public acceptance of this CDR approach; it is therefore in the interest of all stakeholders to be transparent in their measurement approaches and to provide a scientific basis and rationale for deployment of EW as a solution to address climate change.

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M. O. Clarkson, C. S. Larkin and P. Swoboda declare that they work for a for-profit company (InPlanet GmbH) deploying enhanced weathering for carbon dioxide removal. J. Campbell sits on the science advisory board for InPlanet.

Author contributions

MOC instigated the article, and wrote the first draft. CSL, TJC, TR, CNM and TJS all contributed and wrote sections, with all authors contributing to the final version. All authors approved the submitted version.

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Figures

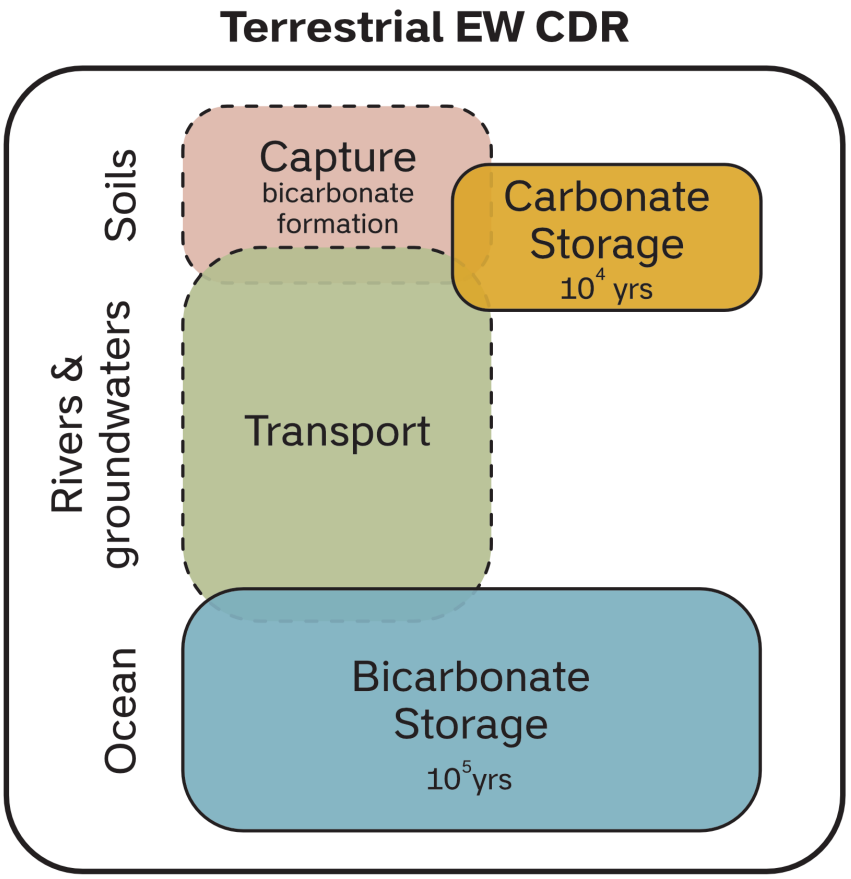

Fig 1. Illustration of conceptual stages for terrestrial EW CDR. The open system processes can be broadly separated into three stages; i) capture, ii) transport and iii) storage. Note that there is spatial and temporal overlap between the stages. The different stages give a modularity to CDR measurement where we focus here on soil processes, with methods to estimate the primary capture stage of bicarbonate formation.

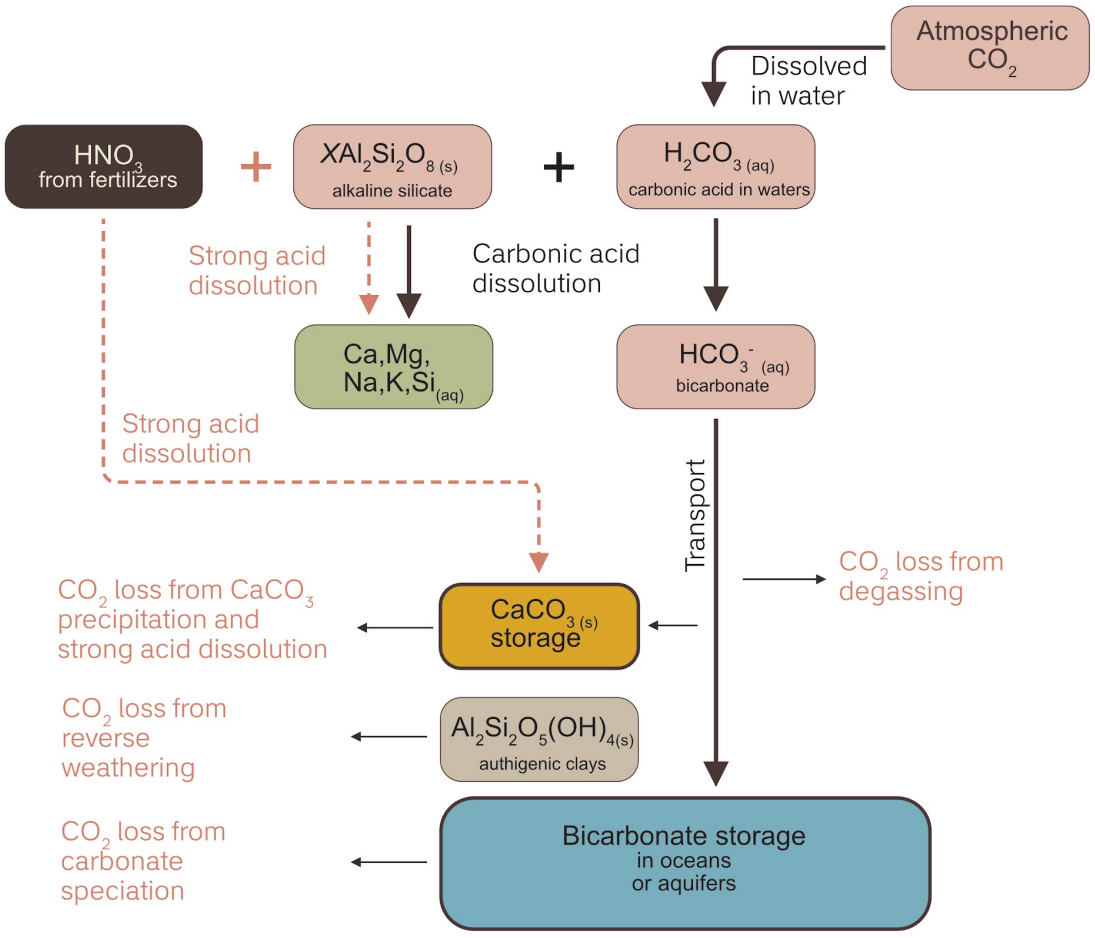

Fig. 2 Summary of the weathering process and potential complicating processes that result in downstream CO2 loss. The primary aim of measurement techniques are to trace the loss or gain of weathering products in different phases; solid, liquid or gas. This can be relatively straightforward in cases where carbonic acid is the dominant weathering acid, but in cases where fertilizers produce nitric acid, weathering products may be released without concomitant CO2 removal. Strong acids also drive carbonate dissolution that is a CO2 source. CO2 can also be lost during transport and at the final storage location, however a detailed review of these processes is beyond the scope of this paper.

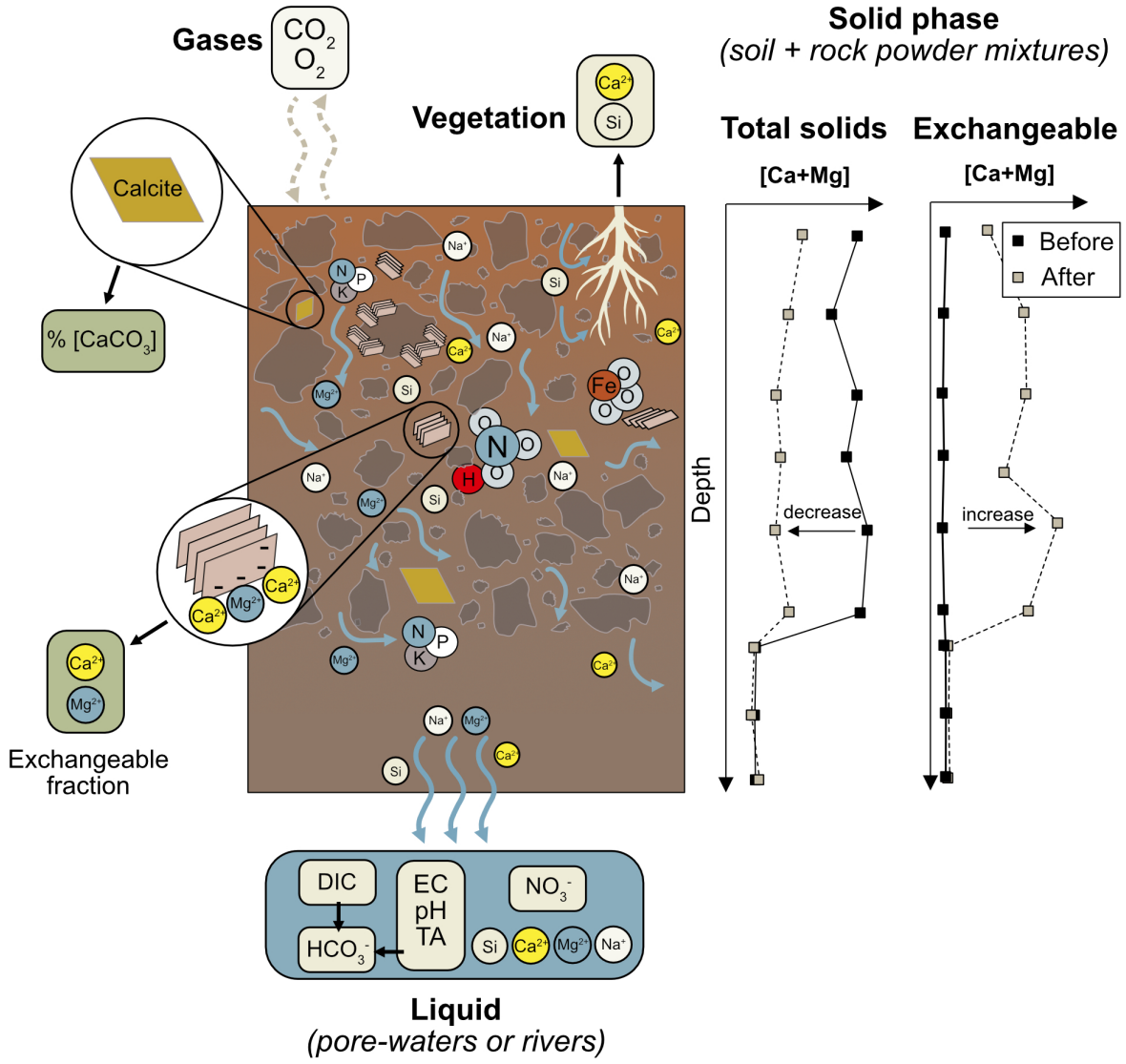

Fig. 3 Illustration of cation mass balance rooted in the concentration of an immobile trace element, Ti, modified from Reershemius, Kelland et al. (2024). Start and end values serve illustration purposes only and have not yet been measured. Here we show Mg as an example of a mobile cation, j. Panel A demonstrates the mixing line created by the baseline soil plus rock powder, where any combination of soil + rock powder would fall on this mixing line. B illustrates how a measure of immobile Ti at the end of weathering ([Ti]end) can be used to calculate [Mg]add. C illustrates the loss of [Mg] during weathering, gained by the measurement of $[Mg]_{end}$, and is expressed as the change in [Mg] (Δ[Mg]). D demonstrates the cases where application amounts vary and weathering rates remain the same, meaning the fraction of [Mg] lost relative to $Mg]_{add}$ (Fd), remains constant (dashed lines). Three examples are shown for no weathering (Fd=0), majority weathering (Fd=0.7) and complete weathering (Fd=1). Erosive loss of powder would be effectively the same as variable powder addition (D), illustrated by the sample moving toward $[Mg]_{soil}$, $[Ti]_{soil}$ with a slope of approximately constant Fd.

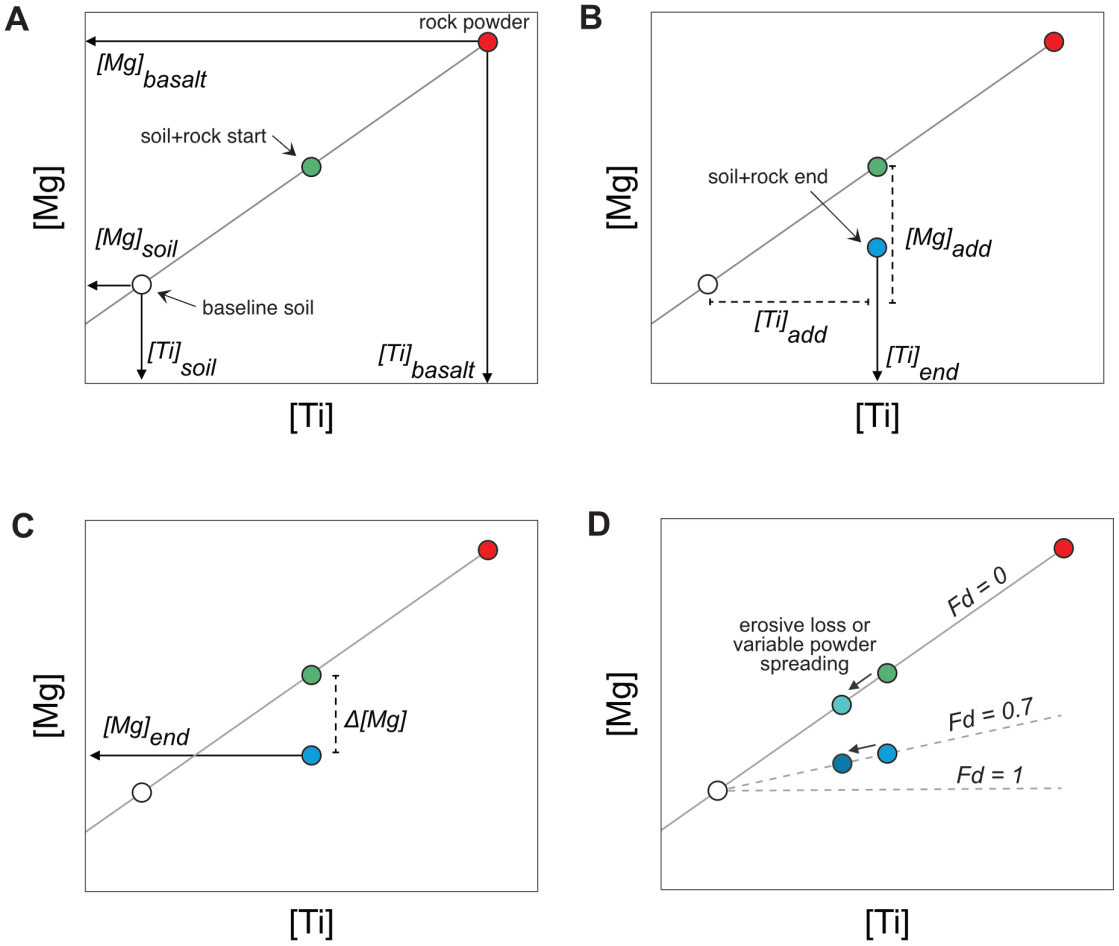

Fig. 4 Schematic view of approaches to monitoring weathering activity and idealized examples of total solid and exchangeable results. Different measurement pathways illustrate different components of the weathering mass balance, which must be comprehensively quantified to estimate weathering rates and calculate CDR. Data serve an illustrative purpose only and are not based on measurements.

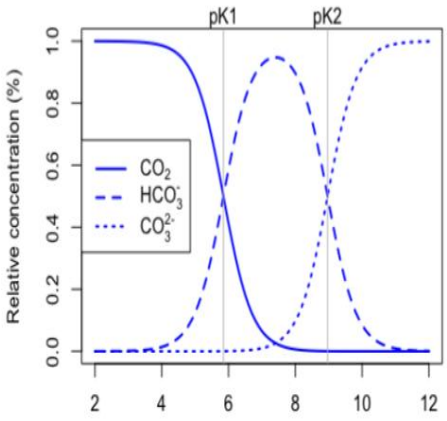

Fig. 5. Bjerrum plot (created in RStudio with package seacarb and default values (Zeebe and Wolf-Gladrow, 2001) showing the relative concentrations of carbonate species in solution. The typical pH range for natural waters is indicated, where the dominant species of dissolved inorganic carbon is HCO_3^-.

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Tables

Table 1 Comparison of the main methods to quantify EW. Methods are organized by the sample most commonly required to make the measurement type

Phase	Section	Basis	Advantages	Disadvantages
Solid samples	**2.2.1 Maximum CDR potential of the feedstock**	Uses the concentration of alkaline oxides in the feedstock to determine maximum amount of CO_2 that could be stoichiometrically removed through dissolution	Useful for first considerations of feedstock choice	No temporal component Assumes complete weathering No consideration for acid type or CO_2 losses
	2.2.2 Solid phase element mass balance	Examines cation concentrations in soil+rock powder mixtures to identify the loss of cations through dissolution. Cations measured in reference to immobile elements that remain in the soil.	Sampling soils aligns with agronomic practices Temporally integrated signals	Limited by measurement precision Limited by soil heterogeneity which can lead to large uncertainties No consideration for acid type or CO_2 losses
	2.2.3 Accumulation of soil inorganic carbon	Measures the build up of soil inorganic carbon, which is one storage pool for capture carbon	Measure of captured and stored carbon via mineralization pathway Well established and standardized protocols	Does not include an estimate of bicarbonate capture or storage Limited to settings where carbonate precipitation occurs No consideration for acid type or CO_2 losses
	2.3 Accumulation of	Quantifies cations that are temporarily stored in soil exchange sites	More clearly resolved differences compared to	Non-standardised chemical treatments, highly dependant on soil types

	weathering products in exchangeable phases		total solids	No consideration for acid type or CO_2 losses Temporal fluctuations may bias/limit signals Assumes no leaching of cations occurs between sample intervals; cations lost to groundwater will not be detected as CDR
Liquid samples	**2.4.2 Base cations and dissolved silica**	Quantifies the amount of rock powder dissolved by measuring the accumulation of weathering products in liquid samples (soil waters or rivers)	Accurately identify flux of weathering products Spatially integrated if sampling rivers/drainage channels	Does not consider cations lost to the exchangeable fraction In some instances, limited scalability due to operational requirements Temporal fluctuations may bias/limit signals
	2.4.3 Anions	Quantifies bicarbonate accumulation in liquid samples (soil waters or rivers)	Direct measure of bicarbonate Identify non carbonic acids	In some instances, limited scalability due to operational requirements Temporal fluctuations may bias/limit signals
	2.4.4 Total alkalinity, pH and DIC	Proxy measurement for bicarbonate accumulation in liquid samples (soil waters or rivers)	Closely linked to bicarbonate concentration	Labour/skill intensive requiring careful sample handling Temporal fluctuations may bias/limit signals Can be influenced by respiration

	2.4.5 Electrical Conductivity (EC)	Proxy measurement for total ion activity in liquid samples (soil waters or rivers)	Can be measured by sensors	Requires calibration of EC to alkalinity or cation concentrations
	2.5.2 Stable carbon and oxygen isotopes **2.5.3 Radiocarbon** **2.5.4 Radiogenic strontium**	Use isotope signatures to inform on the weathering mass balance (quantify sources and sinks)	Informs on additionality (i.e. C derived from non-air sources)	Some are expensive (radiocarbon) Complex interpretation
	2.5.5 Novel isotopes (Li, Mg, Si, stable Sr)	Use isotope signatures to inform on the weathering mass balance (quantify sources and sinks) and secondary processes	Detailed information on reaction processes, sources and sinks	Expensive Complex interpretation
Gas samples	**2.6 Gaseous phases**	Directly measurement of CO_2 efflux in the soil system	Potential direct, in-situ measurement of CDR Can be combined with other GHG fluxes	Temporal fluctuations may bias/limit signals Dominated by organic carbon cycle and transient or short term carbon cycling

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