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Initial Validation of a Soil-Based Mass-Balance Approach for Empirical Monitoring of Enhanced Rock Weathering Rates

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mesocosms. In our experiment, a basalt rock feedstock is added to soil columns containing the cereal crop *Sorghum bicolor* at a rate equivalent to 50 t ha⁻¹. Using our approach, we calculate rock weathering corresponding to an average initial CDR value of $1.44 \pm 0.27 \text{ tCO}_2\text{eq}$ ha⁻¹ from our experiments after 235 days, within error of an independent estimate calculated using conventional elemental budgeting of reaction products. Our method provides a robust time-integrated estimate of initial CDR, to feed into models that track and validate large-scale carbon removal through ERW.

KEYWORDS: enhanced rock weathering, carbon dioxide removal, negative emissions technology, monitoring, reporting, and verification, climate change mitigation

1. INTRODUCTION

Avoiding 2 °C of global warming by 2100 will require a dramatic reduction in carbon emissions, meaning governments must implement policies with increasingly stringent year-on-year carbon mitigation targets.^{1,2} Even the full implementation of all emissions mitigation policies, as of 2022, will result in a 12 Gt (10^9 t) CO₂ equivalent shortfall to climate goals as outlined by the Paris Agreement.³ In the absence of feasible pathways for sufficiently reducing carbon emissions, large-scale carbon dioxide removal (CDR) will likely be essential for augmenting decarbonization efforts in the coming century (e.g., refs 4 and 5).

Enhanced rock weathering (ERW) is a promising CDR technique in which naturally occurring mineral weathering reactions that consume atmospheric CO_2 are accelerated. This may be achieved by applying crushed silicate rocks with a large reactive surface area to agricultural and forest soils (e.g., refs 6–21). Potential advantages and co-benefits of ERW include a low technological barrier to implementation at scale,^{8,13} long-term storage of carbon compared to organic reservoirs (>10 000 years),^{22–28} and a supply of key nutrients for crop

growth.^{13,29–37} Additionally, ERW feedstocks such as basalt may be used for the deacidification of soils, filling the role of agricultural lime (currently seen as a net source of CO_2 to the atmosphere^{38–46}). Our understanding of ERW has been improved by recent work on mechanistic modeling of weathering reactions in agricultural soils (e.g., refs 11, 14, 47, and 48), modeling hydrological effects on weathering rates (e.g., ref 49), laboratory and mesocosm experiments tracking uptake of nutrients by plants and feedstock dissolution rates (e.g., refs 31, 33, 46, and 50–56), and field experiments implementing ERW at scale (e.g., refs 35 and 57–60).

Despite these recent advances, ERW currently lacks a robust and widely accepted framework for monitoring, reporting, and

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Figure 1. TiCAT conceptual framework as a simple two-component mixing model. (a) Idealized soil and basalt (a commonly proposed ERW feedstock) end member compositions plotted in [Ti] vs [CAT] space. (b) A mixture of soil and basalt initially falls on the idealized mixing line between both end members. (c) Dissolution results in a decrease in [CAT] of the mixture, while [Ti] is conserved as Ti is immobile; the original composition of the soil/basalt mixture (indicated by the white circle) is the intersection of [Ti]_{end} with the mixing line, and Δ [CAT] correspond to the amount of CAT lost by dissolution.

verification (MRV) of CDR rates. This represents a significant barrier to widespread implementation of ERW, in voluntary or compliance markets or as a subsidized agronomic practice. There will be strong variability in the rates of rock weathering in agricultural settings with variable hydroclimatic conditions, highlighting the need for empirical constraints on weathering at this stage (e.g., ref 61). Approaches to MRV that are entirely model-based are yet to be fully validated for ERW. The current generation of reactive transport models for simulating ERW has proven to be useful for making testable predictions (e.g., refs 14, 19, 47, and 48). However, it is not yet clear whether such models are capable of accurately predicting CDR on a deployment scale. Therefore, any modeling approach to estimate CDR through ERW at scale must have at its center a robust empirical MRV framework from a diverse set of environments to impart confidence to key stakeholders. The MRV framework must successfully report site- and timespecific rates of feedstock weathering while being cost-effective and minimally invasive (e.g., refs 62 and 63).

To quantify weathering rates and/or initial CDR rates from ERW experiments, previous mesocosm and field studies have used measurements of soil inorganic carbon (e.g., refs 33, 55, 57, and 59); the concentration of dissolved ions in porewaters and effluent waters, including cations such as Ca²⁺ and Mg²⁺, as well as carbonate alkalinity (e.g., refs 31, 33, 50-54, 56, 58, 59, and 64); and Sr, Li, Mg, and C isotopic analysis of waters, soils, and rocks (e.g., refs 33, 51, 52, 59, and 64). These data provide valuable insight into the rate of weathering of feedstocks and the fate of reaction products at different stages of transport from topsoil to the river-ocean system, and it is therefore important that such measurements be made for a representative range of ERW deployment scenarios. However, basing a site-specific empirical MRV protocol on these metrics is challenging. Significant carbonate precipitation in soils is unlikely to occur within the pH range of most agricultural soils that require amendments for deacidification (as well as being undesirable), and collecting porewater and effluent water for analysis of field-specific weathering rates is time- and laborintensive and at watershed scale is feasible in only limited settings, such as zero-order streams (e.g., ref 59). For these reasons, such measurements likely cannot be used in every ERW deployment if the technology is to scale.

Recent work using measurements of soil exchangeable cations and electrical conductivity as proxies for weathering and alkalinity generation, respectively, has been a welcome step toward building an MRV tool kit that meets the criteria for providing an empirical base in a wide range of agricultural ERW deployments, by tying in to existing agronomic practices or introducing practices that can be easily scaled.^{60,65} However, there can be large errors associated with tracking alkalinity fluxes through electrical conductivity (see refs 65 and 66), while calculating weathering rates purely from the size of the soil exchangeable fraction presents a minimum weathering estimate.

Here, we add to this tool kit by introducing and providing an initial proof-of-concept study of a soil-based mass-balance approach for quantitatively tracking ERW in soils. This approach measures the difference in concentration of the ERW feedstock within a soil in situ before and after weathering, directly building from techniques widely used to gauge the extent and mode of weathering in natural systems (e.g., refs 67-79). We compare the concentrations of mineral-bound metal cations $(Ca^{2+}, Mg^{2+}, and Na^{+})$ in the solid phase of soils before and after feedstock deployment. We do this by estimating changes in the total amount of these metal cations (CAT) in a specific soil sample relative to the concentration of an immobile tracer, in this case titanium (Ti). Hereafter, we refer to this method as TiCAT. As a first step toward robust validation, we compare estimates of the extent of in situ basalt feedstock dissolution from TiCAT to rates determined independently from detailed pool and flux tracking (>2000 measurements) in a mesocosm experiment (following a method similar to that in ref 33). We then discuss the practical considerations for this approach to be scaled for industrial-scale deployment of CDR through ERW, and the steps required to move from an empirical estimate of feedstock dissolution rates to robust error-bounded estimates of CDR.

2. MATERIALS AND METHODS

2.1. Theoretical Basis. TiCAT is a mass-balance approach for estimating the time-integrated amount of weathering of a rock feedstock, in this case basalt, within a soil sample. This method builds on approaches for estimating the extent of weathering in natural systems, where the concentrations of mobile major cations in an unweathered parent material are

compared to those in an equivalent amount of weathered material. The concentration of an immobile trace element is used to establish this equivalence (e.g., refs 67–79; see also Supporting Information section 1.9). In ERW deployments, the unweathered parent material (basalt feedstock) is mixed into the soil. This presents a challenge, as in a field setting, the amount of basalt present in a soil sample taken after deployment will not necessarily be proportional to the total amount of basalt deployed, given soil mixing may not be perfectly homogeneous, and some erosion may occur.

To calculate the amount of unweathered parent material initially present in a sample taken after weathering of some of this material has occurred, we first compare soil samples after basalt amendment and weathering with soil samples representative of a pre-amendment baseline, as well as samples of the initial basalt feedstock. This can most readily be visualized as simple two-component mixing between a soil (c_s) and a basalt (c_b) end member (Figure 1a). We use the difference in the concentration of an immobile trace element [e.g., Ti, which is widely used for this purpose (see refs 70 and 80)], between a postapplication sample (c_{end}) and the preapplication soil baseline to calculate the amount of basalt that has been added to the original soil for the specific sample analyzed $([Ti]_{end} - [Ti]_s = [Ti]_{add})$. The assumption of immobility is critical to this approach, so while other elements could be used instead of Ti, it must be demonstrated that this criterion is met (see Supporting Information section 1.9).

Using the relative abundance of Ti and mobile major cations (CAT) in the original basalt feedstock, we can then calculate the corresponding concentration of mobile major cations, $[CAT]_{add}$, from the basalt feedstock present in the soil/basalt mixture at the point of basalt application (Figure 1b). For a generic cation, CAT

$$[CAT]_{add} = [Ti]_{add} \times \frac{[CAT]_b - [CAT]_s}{[Ti]_b - [Ti]_s}$$
(1)

Subtracting the concentration of cation in the postapplication sample, $[CAT]_{end}$, and adding the soil baseline, $[CAT]_{s}$, we can calculate the difference in the concentration of the mobile cation, $\Delta[CAT]$, between the expected concentration from addition of basalt and the observed concentration in the soil/ basalt mixture after weathering (Figure 1c):

$$\Delta[CAT] = [CAT]_{add} + [CAT]_{s} - [CAT]_{end}$$
(2)

 Δ [CAT] therefore represents cation lost during to basalt dissolution (i.e., exported from the solid phase) between the point of basalt application and the postapplication sampling date. We can also define basalt dissolution as a fraction, $F_{\rm D}$, where

$$F_{\rm D} = \frac{\Delta [\rm CAT]}{[\rm CAT]_{\rm add}} \tag{3}$$

The concentration of Ti and CAT in samples may be affected by basalt dissolution, reducing the mass of the system. Therefore, a correction for mass loss is applied to F_D (see Supporting Information section 1.9). Multiplying corrected F_D for each cation by the application rate of basalt-hosted CAT gives a cation-specific estimate for weathering of the basalt feedstock at the application scale, assuming that the extent of weathering in an individual sample is representative. Variability in hydrology and soil characteristics (e.g., ref 81) means that at field scale, it is likely that multiple samples from sites representative of a range of field conditions (pH, density, etc.) will need to be analyzed for a representative weathering estimate to be calculated.

From the calculated in situ cation-specific weathering rates of basalt feedstock, an initial rate of CDR (i.e., conversion of carbonic acid to bicarbonate) can be calculated, assuming the acidity consumed during silicate mineral dissolution is ultimately sourced from atmospheric CO₂ (see Supporting Information section 1.9 for more details). In many agricultural settings, fertilizer amendments such as urea ammonium nitrate (UAN) are used. Nitrification of reduced nitrogen species is a source of strong acid, which can also contribute to mineral weathering. In this case, feedstock weathering may result in CDR. In cases in which the strong acid would have interacted with a silicate mineral already, this weathering needs to be discounted from initial CDR estimates (see Supporting Information section 1.10). The initial CDR rates calculated can be considered to be the maximum possible CDR from an ERW deployment and do not take into account downstream processes that will reduce the efficacy of carbon storage as bicarbonate in the river-ocean system, such as re-release of CO₂ via the precipitation of secondary clays and carbonates outside the soil column, or potential degassing of CO2 after conversion of bicarbonate to carbonic acid by reequilibration in acidic solutions (e.g., refs 20, 63, and 82-84).

2.2. Analytical Requirements. The resolvability of a dissolution signal from soil-based mass balance is a function of analytical uncertainty, feedstock application rate, and extent of feedstock dissolution. Reducing uncertainty on instrumentation used to analyze elemental composition is a critical aspect of the TiCAT approach and is likely to be a critical issue for any other approach aiming to track CDR from the solid phase. This is due to the signal-to-noise ratio associated with measuring a small amount of feedstock mixed into a large amount of background soil. For technically and commercially feasible feedstock application rates [likely <50 t ha⁻¹ (see ref 13)], analytical uncertainty can result in overlap between errorbounded values for cation concentration of soil/feedstock mixtures before and after dissolution has occurred. Using representative soil and basalt compositions from this study for instance, at 5% analytical uncertainty (a typical lower bound for global analytical uncertainty in X-ray fluorescence measurements of major element concentration in soils; see, e.g., refs 85-87 and Supporting Information section 1.7) a 25% loss of major cations from the basalt portion of a soil/feedstock mixture is unresolvable even at an application rate of 100 t ha^{-1} , assuming the mixture is homogenized to a depth of 10 cm (a common mixing regime for managed row crop systems). However, at 1% analytical uncertainty, the same extent of cation loss can be resolved at ~ 25 t ha⁻¹ (Figure 2). Accounting for a range of plausible dissolution and application rates, analytical uncertainty must generally be limited to $\sim 1\%$ for our mass-balance method to be accurate and widely applicable, a standard that is more stringent than what is currently be achieved by most commercial inorganic elemental analysis, including commercial mass spectrometry (e.g., refs 88 and 89).

We obtain the requisite analytical precision for applying the TiCAT method here by using isotope-dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). Isotope dilution is a well-established analytical method in which the concentration of an element in a sample can be measured from the known concentration of an element in a spike solution and



Figure 2. Mixing model with representative data for soil and basalt feedstock end members. Assumed homogeneous soil/basalt mixtures from basalt addition and mixing to 10 cm depth are shown for a range of basalt application scenarios (see the inset, b). Error envelopes are shown for the mixing line and a line indicating theoretical 25% dissolution, based on uncertainty in measuring the elemental concentration of soil and soil/basalt samples. The resolvability of a dissolution signal is dependent on dissolution rate, basalt application rate, and analytical error. The mixing line error envelope assumes that the absolute analytical error of basalt is the same as that of soil, a realistic scenario given repeat measurements of a bulk feedstock; the dissolution error envelope assumes that sampling gives a representative soil background.

the ratios of two isotopes of the same element in the natural sample and the spike.^{90–92} The amount of an element in the sample, $n_{\rm sam}$, is given by

$$u_{\rm sam} = n_{\rm spk} \frac{R_{\rm spk} - R_{\rm mix} \sum_{i} R_{i\rm sam}}{R_{\rm mix} - R_{\rm sam} \sum_{i} R_{i\rm spk}}$$
(4)

where R is the ratio of two isotopes and $\sum_i R_i$ is the sum of ratios of all isotopes to a reference isotope (e.g., ref 90; see also refs 91 and 92). We used an isotope spike "cocktail", doped with isotopes of Mg, Ti, and Ca found in lower abundance in natural samples (Figure S5). Isotope spikes were prepared from powders of spiked TiO₂, MgO, and CaCO₃. The pure spike Ca carbonate powders were digested using HCl, and the Mg and Ti oxide powders were digested using HNO₃, HCl, and HF. Following the digestion, each spike solution was calibrated by measuring the relative concentration of Mg, Ca, and Ti isotopes on a Thermo Scientific Neptune Plus multicollector ICP-MS instrument for ~48 h. Estimates of the uncertainty on the spike determination were <0.1% based on replicate analysis. Individual spike solutions were then used to make an isotope spike "cocktail" solution containing Mg, Ca, and Ti spikes. The "cocktail" was added to each sample during the dissolution stage of sample preparation to ensure sample-spike equilibration.

Isotope dilution allows for sample-specific calculation of element concentrations, unlike a typical calibration curve method, whereby calibration standard solutions at known concentrations are run to relate element intensities (in counts per second) to concentration. Isotope dilution therefore corrects for matrix effects, mass bias, and instrument drift and thus improves the accuracy and precision of measured concentrations, significantly reducing global analytical uncertainty (Figure 3; see also ref 93). In addition to an iCAP TQ ICP-MS instrument used to run samples for this study, we analyzed certified reference materials (BHVO-2 basalt and SGR-1b shale) on other ICP-MS models to test the data quality achieved by a variety of widely available instruments (a PerkinElmer NexION 5000 Multi-Quadropole ICP-MS instrument and a Thermo Scientific ElementXR High Resolution Magnetic Sector ICP-MS instrument). For sample runs on the iCAP TQ ICP-MS, we were able to achieve average analytical uncertainty on reference materials of 0.22% for Ti, 0.78% for Mg, 0.39% for Ca, and 0.58% for Na (not using isotope dilution), when calculating uncertainty as the mean difference of calculated to certified values (global analytical uncertainty), and 0.75% for Ti, 1.16% for Mg, 1.29% for Ca, and 2.54% for Na (not using isotope dilution), when calculating uncertainty



Figure 3. Representative analytical error for Ca, Mg, and Ti on standards run on three different ICP-MS instruments, using a calibration curve method and an isotope-dilution method. Isotope dilution cannot be used to calculate concentration of Na as it has a single stable isotope. The gray shaded region represents an analytical error range of \pm 1%. The ICP-MS instruments that were used were two quadropole instruments (Thermo Scientific iCAP TQ ICP-MS and PerkinElmer NexION 5000 Multi-Quadropole ICP-MS) as well as a Thermo Scientific Element High Resolution Magnetic Sector ICP-MS instrument.



Figure 4. Initial CDR estimates calculated using cation data from TiCAT and from non-mineral-bound cation budgets. Results are shown (a) for individual mesocosms and (b) as mean values for all mesocosms pooled by treatment type, where dark gray bars show all basalt-treated mesocosms as a single pooled data set. Error bars for TiCAT are the propagated analytical error in panel a, and standard errors of means $(\pm \sigma)$ where baseline soil and basalt samples have been pooled. Error bars for the approach using leachate, plant, and soil extraction budgeting approach are the propagated standard errors between measurements for all mesocosms of the same treatment in panel a, and standard errors of the mean $(\pm \sigma)$ where baseline soil and basalt samples have been pooled.

by the standard deviation of measurements as a percentage of the mean. Our results show that isotope dilution allows for a level of measurement accuracy and precision on quadrupole ICP-MS instruments that would otherwise typically only be achievable with a magnetic sector instrument. Given its much lower cost and far greater availability, the ability to leverage quadrupole ICP-MS for rapid, high-throughput analyses may ultimately be a critical factor in making this MRV technique economically viable at scale.

2.3. Mesocosm ERW Experiments. As an initial test of the TiCAT method, we employed laboratory mesocosm ERW experiments, which allowed us to independently estimate ERW and CDR by measuring the concentration of reaction products in plant, soil exchangeable fraction, and leachate solution pools (see refs 29, 31, 33, 50-54, 56, and 59). Each mesocosm contained a single C4 cereal crop Sorghum bicolor plant (see ref 33) with two different fertilizer treatments: nitrogenphosphorus-potassium (NPK) (n = 14) or manure (n = 14)14). Basalt feedstock equivalent to an application rate of 5 kg m^{-2} (50 t ha⁻¹) was added to half of the columns for each fertilizer treatment, mixed to a depth of 12 cm. All columns were left in a controlled environment for 235 days (for a detailed description of mesocosm design and construction, substrate and feedstock preparation and characterization, plant varieties and growth conditions, and irrigation regime, see the Supporting Information).

Leachate was collected from mesocosms at six discrete leachate events, accounting for the entire leachate flux during the experiment. After 235 days, samples were taken from relevant chemical pools: the soil exchangeable fraction, the solid phase with the exchangeable fraction removed by leaching with ammonium acetate, and the plant material (comprising shoots, roots, and seeds). Analysis of total inorganic carbon (TIC) did not show detectable increases in

a subset of mesocosm soils tested before leaching with ammonium acetate (using an Eltra C/S analyzer with a detection limit of 0.1 wt % C), suggesting that carbonate formation should have a negligible impact on the overall cation budget of the mesocosm systems. Aliquots of solid phase samples were then ashed and digested using HNO₃, HCl, and HF, and elemental concentrations measured using ID-ICP-MS (see Supporting Information section 1.7). Using a conventional approach focused on reaction products, we calculated elemental budgets for major cations for each mesocosm from the dissolved or non-mineral-bound pools (leachate, soil exchangeable fraction, and plant material) (see Supporting Information section 1.8). We compared the elemental budgets calculated for basalt-amended mesocosms to those of a control mesocosm for each fertilizer treatment that had no basalt applied. Control mesocosms were selected as the control replicates for which the topsoil major element composition most closely matched the initial soil baseline. Excess Na⁺, Ca²⁺, and Mg²⁺ in the elemental budget of basalt-amended mesocosms relative to the controls were assumed to represent the reaction products of basalt dissolution. From the amounts of these cations, we obtained the initial ERW rates. Using a modified Steinour formulation, a simple stoichiometric approach that relates the amount of mobile cations to the amount of carbonic acidity converted to bicarbonate by charge balance (see Supporting Information section 1.3), ERW rates were converted to initial CDR estimates.

These rates can be compared with those obtained using the TiCAT method, as the cations released into non-mineralbound pools from feedstock weathering should correspond to the amount of cation loss from the basalt fraction being weathered. We analyzed the concentration of Na, Ca, Mg, and Ti in the solid phase samples taken from the upper 12 cm portion of each mesocosm. We calculated the $F_{\rm D}$ of the basalt fraction present in the soil/basalt mixture separately for each major cation and corrected these for the concentration effect from basalt dissolution (see section 2.1 and Supporting Information section 1.9). From the corrected cation-specific $F_{\rm D}$ for each mesocosm and using the application rate of basalt for each mesocosm, we calculated the total amount of major cations in basalt applied over a given area that was dissolved (see Supporting Information section 1.9), giving an initial ERW rate, and using the same modified Steinour formulation as described above, an initial CDR estimate. To directly compare the TiCAT method to a weathering product approach, we applied a correction to the TiCAT estimates to account for strong acid weathering from nitrification of fertilizers (Supporting Information section 1.10).

3. RESULTS AND DISCUSSION

Our results generally show agreement between two independent methods of calculating weathering and initial CDR in our mesocosm systems (Figure 4a). The more conventional approach, measuring cation reaction products in dissolved cation pools, yielded mean initial CDR estimates of 1.68 \pm 0.11 tCO₂eq ha⁻¹ (NPK-fertilized) and 1.05 \pm 0.15 tCO₂eq ha⁻¹ (manure-fertilized) across all mesocosms. The TiCAT mass-balance approach introduced here, which measures the loss of cations from the solid phase of soil samples, gave mean initial CDR estimates of 1.84 \pm 0.37 tCO₂eq ha⁻¹ (MPK-fertilized) and 1.04 \pm 0.37 tCO₂eq ha⁻¹ (manure-fertilized). Thus, mean initial CDR estimates from the TiCAT method were within error (±standard error of means) of those from the reaction product method for both NPK- and manure-fertilized basalt-amended mesocosms.

Mean initial CDR values across all basalt-amended mesocosms were 1.44 \pm 0.27 tCO₂eq ha⁻¹ (TiCAT) and 1.36 ± 0.12 tCO₂eq ha⁻¹ (dissolved pools) (Figure 4b). This is broadly consistent with estimated CDR values calculated for similar ERW studies, albeit these range greatly in application amount and duration (see ref 34). Given a CDR potential for the basalt used in our study of 183.56 kgCO₂ t^{-1} (see Supporting Information section 1.3), the initial CDR after carbonic-acid-driven weathering for 235 days was $15.7 \pm 3.1\%$ of this potential, using results from TiCAT. Our results thus demonstrate that the solid phase approach underlying TiCAT produces estimates for initial CDR within error of those calculated by analyzing the dissolved, plant, and soil exchangeable cation pools that constitute the ultimate reaction products in our mesocosm experiments, suggesting that it can yield an accurate and robust estimate of initial CDR in enhanced weathering systems.

It is important to emphasize that the CDR rate estimated based on the time-integrated amount of feedstock dissolution and cation loss should be regarded as only an initial CDR value. There is potential for leakage of initially captured carbon downstream of a given field deployment, as alkalinity and dissolved inorganic carbon are transported from the soil column to the oceans (e.g., refs 20, 63, and 82–84). In addition, a large fraction of the dissolved cation load in any soil will be transiently hosted in soil exchange sites (e.g., refs 94–97; see also ref 56). This cation storage at exchange sites is temporary, and upon their release, dissolved cations will drive CDR through charge balance in the carbonic acid system (see refs 51 and 52). However, this means that there is a variable lag time between feedstock dissolution and CO_2 capture that needs to be considered for accurate CDR quantification. Given these factors, a robust, "cradle-to-grave" MRV approach with TiCAT at its core will also require modeling the transport of weathering products through the soil^{14,19,47,98} and ground-water-river-ocean system^{20,82-84} to determine potential leakage through re-release of CO₂ back to the atmosphere. In the near term, developing and testing these models should be done in conjunction with monitoring of aqueous geochemistry alongside soil-based approaches (such as TiCAT). As with all CDR techniques, emissions accounting must also be implemented to calculate the net CDR rates.

There are several key challenges that need to be met before TiCAT can be widely applied. First, it must be demonstrated that scaling from weathering rates at specific sampling points to a larger system allows for a representative measurement of weathering across that system while minimizing uncertainty. This study suggests that this condition can be met, at least when averaging across mesocosm experiments. Second, spatial heterogeneity of elemental concentrations in managed soils must be examined to assess the density and volume of sampling that must be implemented to be able to directly compare between samples of background soil before ERW feedstock amendment and post-amendment soil; in both cases, specific sampling protocols such as pooling and/or gridded sampling may be useful tools in making representative measurements,⁸¹ and control sites will be useful for testing these. A complication is that in open systems such as agricultural fields, material may be introduced from external sources that could interfere with the simple two-member mixing model (e.g., flooding events and windblown dust). In addition, in some settings other soil amendments may be used in conjunction with silicate minerals. If these contain significant amounts of major cations or the immobile tracer, a more elaborate mixing model must be used to account for these. Additionally, the TiCAT approach may not be viable as a stand-alone MRV framework in specific cases: for example, in settings with a very high degree of physical erosion; in settings where there is significant and fast weathering from soils; in settings where feedstocks are used that have a chemical composition very similar to that of the soil or have lower concentrations of all immobile trace elements; or in settings where feedstocks are especially slow-weathering, such as in arid settings not conducive to ERW. Other site-specific conditions may require alterations to workflows; for example, the depth of sampling required may vary in response to variable mixing depths, as modulated by tilling practices, crop type, and biological mixing.

Lastly, effective implementation of the TiCAT approach relies on stringent constraints on analytical error, which may be challenging via standard practice with most commercially available measurements for elemental concentration, including ICP-MS (see refs 88 and 89). Nonetheless, here we have demonstrated that it is possible using isotope dilution on a standard quadrupole ICP-MS instrument to minimize analytical error to $\sim 1\%$, making even <10% basalt dissolution analytically resolvable for total feedstock application rates of 50 t ha⁻¹. However, the replication of this analytical precision in commercial laboratories will require adjustment to workflows and standard operating procedures. It is also likely that the aggregate impact on unit cost (dollar cost per ton of CO₂ captured) of TiCAT as an MRV procedure will broadly follow a "learning curve" trajectory, driving lower costs as ERW is scaled up (e.g., ref 99).

The TiCAT method overcomes some of the issues with prior methods of estimating ERW, particularly those that rely on accurately measuring the amount and transport of weathering reaction products (i.e., bicarbonate ions, HCO₃⁻, or cations in soil drainage waters) after feedstock application. Methods that rely on tracking the dissolved phase are extremely time- and labor-intensive, introducing significant barriers to scale. For example, a thorough study of a field-scale ERW trial monitoring aqueous reaction products, such as that conducted by ref 59, involves many months of labor- and timeintensive sampling of soils, plants, and possibly porewaters from the agricultural plots onto which ERW feedstock is applied and a wider detailed monitoring of the drainage regime and watershed around such a site. Even using this style of sampling protocol, the necessary granularity of measurements would likely miss short-term fluctuations such as wash-out after rain events, which in many river systems account for an important component of the overall solute discharge (e.g., ref 100). Such measurements, as well as those reliant on directly measuring soil exchangeable cations, can also be complicated by varying time frames over which cations are bound to exchangeable sorption sites within a soil (see refs 51 and 52).

Our approach also directly overcomes possibly the largest uncertainty in scaling ERW in agricultural settings: estimating the initial extent of feedstock dissolution in soils (see, e.g., refs 34 and 61). There is currently significant uncertainty about how rock grain surface areas evolve through time within a given field setting (i.e., individual farm) and the extent to which secondary mineral formation on the surface of the feedstock has the potential to alter mineral dissolution rates (e.g., refs 101–109). In addition, bulk mineral dissolution kinetics are in some cases poorly constrained (e.g., refs 105, 110, and 111). Taken together, these considerations make it extremely challenging to accurately forecast feedstock dissolution across a range of deployment regimes with existing reactive transport models alone. ${}^{34,61,101-111}$

A significant additional advantage of this MRV approach is that it can directly integrate into existing agronomic practices. Samples from the uppermost portion of the soil are already regularly taken for nutrient and soil pH analysis (e.g., refs 94 and 112). Importantly, this means that there is already extensive personnel and infrastructure in place that can be leveraged to scale the empirical validation of ERW at minimal cost, in marked contrast to empirical verification of soil organic carbon concentrations (SOC), which requires modified sampling protocols for accurate empirical results. Existing frameworks for carbon storage in agricultural settings are mostly focused on SOC, which does not allow for land owners and land users to include alkalinity generation through practices such as ERW in an estimate of carbon storage. Deployment of ERW at scale requires MRV tools such as TiCAT to be incorporated into these frameworks. This would allow for the combined use of ERW and SOC maintenance to achieve maximum carbon storage depending on local conditions.

In summary, we have demonstrated with mesocosm ERW experiments that a soil-based mass-balance approach, TiCAT, accurately tracks ERW with a basalt feedstock to allow estimation of CDR rates. CDR estimates using TiCAT are within error of those calculated by complete elemental budgeting of weathering reaction products gained in plant and exchangeable cation pools. Using an isotope-dilution method, we can reduce analytical error sufficiently so that a dissolution signal can be resolved in the solid soil phase at reasonable feedstock application rates. Applying the methods used in this study to field-scale trials is a necessary next step in verifying the capacity of TiCAT for MRV of ERW in the field. Additionally, our approach will ultimately need to be augmented by the development of cradle-to-grave MRV approaches that can provide error-bounded estimates of the final CDR. Nevertheless, our results suggest that a soil-based mass-balance method could be a cost-effective and accurate centerpiece of a robust MRV tool kit for deploying ERW at scale.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c03609.

Supporting Materials and Methods (sections 1.1–1.10), Tables S1 and S2, Figures S1–S10, and additional references (PDF)

All raw data (with errors) for the leachate, plant, soil exchangeable fraction, and soil solid phase (XLSX) Input file "mesocosms initial soil 20230219.xlsx", re-

quired to run Matlab script "TiCAT X" (XLSX)

Matlab script (PDF)

Function in text format (PDF)

Input file "feedstocks.xlsx", required to run Matlab script "TiCAT_X" (XLSX)

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Notes

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