

A new soil-based approach for empirical monitoring of enhanced rock weathering rates

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Synopsis: We describe and empirically validate a geochemical mass-balance approach for tracking rates of Enhanced Rock Weathering in soils, a necessary step in scaling up a promising Carbon Dioxide Removal strategy.

Abstract: Enhanced Rock Weathering (ERW) is a promising scalable and cost-effective Carbon Dioxide Removal (CDR) strategy with significant environmental and agronomic co-benefits. A major barrier to the widescale implementation of ERW is a robust Monitoring, Reporting, and Verification (MRV) framework. To successfully quantify the amount of carbon dioxide removed by ERW at scale, MRV must be accurate, precise, and cost-effective. Here, we outline a new mass-balance-based method where metal analysis on soil samples is used to track the extent of *in-situ* alkaline mineral weathering. We show that signal-to-noise issues of *in-situ* soil analysis can be mitigated by using isotope-dilution mass spectrometry to reduce analytical error. We implement a proof of concept experiment demonstrating the method in controlled mesocosms. In our experiment, basalt 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 an average initial CDR value of 1.47 ± 1.09 tCO₂eq 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.

1 Introduction

Avoiding 2°C of global warming by 2100 will require significant carbon emissions reduction. Governments must implement policy with increasingly stringent year-on-year carbon mitigation targets (1, 2). Despite recent progress, the implementation of all current policies will result in a 12 gigatonne (10^9 tonnes) CO₂-equivalent shortfall to climate goals as outlined by the Paris Agreement (3). In the absence of feasible pathways to sufficiently reduce carbon emissions, large-scale Carbon Dioxide Removal (CDR) is essential for augmenting decarbonization efforts in the coming century (e.g., 4, 5).

Enhanced Rock Weathering (ERW) is a promising CDR technique where naturally occurring mineral weathering reactions that consume atmospheric CO₂ are accelerated. Typically, this may be achieved by applying crushed silicate rocks with a high reactive surface area to agricultural and forest soils (e.g., 6-20). 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) (21-27); supply of key nutrients for crop growth (13, 28-33). Additionally, ERW feedstocks such as basalt may be used for the deacidification of soils, filling the role of agricultural lime (currently a net source of CO₂ to the atmosphere; 34-42). Several recent studies have improved our understanding of ERW: mechanistic modelling of weathering reactions in agricultural soils (e.g., 11, 14, 43); modelling hydrological effects on weathering rates (e.g., 44); laboratory and mesocosm experiments tracking uptake of nutrients by plants, and feedstock dissolution rates (e.g., 30, 32, 42, 45-51); and field experiments implementing ERW at scale (e.g., 52-55).

Despite these recent advances, ERW currently lacks a robust framework for Monitoring, Reporting, and Verification (MRV) of CDR rates. This represents a significant barrier to widespread implementation on voluntary or compliance markets. Varying rock weathering rates in agricultural settings with variable hydroclimatic conditions are among the most critical uncertainties associated with carbon dioxide removal in the field (e.g., 56). Approaches to MRV that are entirely model-based are yet to be fully validated for ERW. The current generation of so-called “reactive transport models” for simulating ERW have proven useful for making testable predictions (e.g., 14, 19, 43). However, it is not yet clear whether such reactive transport models are capable of accurately predicting CDR at deployment scale. Therefore, any modelling approach to estimate CDR through ERW at scale must have at its center a robust empirical MRV framework from diverse set of environments to impart confidence to key stakeholders. The MRV framework must successfully report site- and time-specific rates of feedstock weathering while being cost-effective and minimally invasive (e.g., 57, 58). Recent work using measurements of soil exchangeable cations and electrical conductivity as proxies for weathering and alkalinity generation respectively have been welcome steps toward building an MRV toolkit (55, 59). However, there can be large errors associated with tracking alkalinity fluxes through electrical conductivity (see ref. 59, 60). Both practices are also a deviation from typical agronomic practices, potentially providing a barrier to scaling in working farms.

Here, we add to this body of work by introducing and providing a proof of concept study of a soil-based mass balance approach for quantitatively tracking enhanced rock weathering in soils. Our approach measures the difference in concentration of ERW feedstock *in-situ* before and after

weathering. This directly builds from techniques widely used to gauge the extent and mode of weathering in natural systems (e.g., 61-73). We compare the concentrations of mineral-bound metal cations (Ca^{2+} , Mg^{2+} , 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 towards 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 (see 32). We then discuss the practical advantages of this approach for industrial scale deployment of CDR through ERW, and the steps require to move from an empirical estimate of feedstock dissolution rates to robust error-bound estimates of carbon dioxide removal.

2 Materials and Methods

2.1 Theoretical Basis

TiCAT is a mass balance approach for estimating the time-integrated amount of basalt feedstock in a soil sample that has undergone weathering. This method builds on approaches for estimating the extent of weathering in natural systems (e.g., 61-73). Within the TiCAT framework, this involves calculating changes in the concentrations of major cations in soils that have been amended with basalt, with the assumption that basalt weathering progresses at a much faster rate than that of the background soil.

To define an unweathered parent material, we first compare soil samples after basalt amendment with soil samples representative of a pre-amendment baseline, as well as samples of the basalt feedstock. This can most readily be visualized as simple two-component mixing between a soil (c_s) and a basalt (c_b) endmember (**Fig. 1a**). We use the difference in concentration of an immobile trace element, i (e.g., Ti, though other elements could be used – see *Supporting Information Section 1.10*), between a post-application sample (c_{end}) and the pre-application soil baseline, to calculate the amount of basalt that has been added to the original soil for the specific sample analyzed ($Ti_{\text{end}} - Ti_s = Ti_{\text{add}}$).

Using the relative abundance of Ti and mobile major cations (CAT) in the original basalt feedstock, we can then calculate the corresponding amount of mobile major cations, CAT_{add} , from the basalt feedstock present in the soil + basalt mixture at the point of basalt application (**Fig. 1b**). For a generic cation, CAT:

$$CAT_{\text{add}} = Ti_{\text{add}} \times \frac{CAT_b - CAT_s}{Ti_b - Ti_s} + y \quad , \quad (1)$$

where y is the CAT intercept of the mixing line (Fig. 1). Subtracting the amount of cation in the post-application sample, CAT_{end} , and adding the soil baseline, CAT_s , we can calculate the difference in the amount of the mobile cation, ΔCAT , between the expected amount from addition of basalt, and the observed amount in the soil + basalt mixture after weathering (**Fig. 1c**):

$$\Delta CAT = CAT_{\text{add}} + CAT_s - CAT_{\text{end}} \quad . \quad (2)$$

ΔCAT therefore represents the amount of cation loss due to basalt dissolution (i.e., exported from the solid phase) between the point of basalt application and the post-application sampling date. We can also define basalt dissolution as a fraction, F_D , where:

$$F_D = \frac{\Delta\text{CAT}}{\text{CAT}_{add}} \quad (3)$$

Multiplying F_D for each cation by the application rate of CAT in the basalt feedstock gives a value for ERW which can then be converted into an initial rate of CDR (see *Supporting Information Section 1.10* for more details).

2.2 Analytical requirements

Limiting analytical error 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 adding feedstock to a large mass of background soil. For technically and commercially feasible feedstock application rates (likely 5-50 t ha⁻¹, see 13), analytical error can result in overlap between error-bounded values for cation concentration of soil-feedstock mixtures before and after dissolution has occurred. In our mesocosm experiment for instance, at 5% analytical error 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 10cm (a common mixing regime for managed row crop systems). However, at 1% analytical error the same amount of cation loss is resolvable at ~25 t ha⁻¹ (**Fig. 2**). Thus, when accounting for a range of plausible dissolution and application rates analytical error must generally be limited to ~1% for our mass balance method to be accurate and widely applicable, a standard that is more stringent than that currently achievable by most commercial inorganic mass spectrometry analyses (e.g., 74, 75).

We obtain the requisite analytical precision for applying the TiCAT method using isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). Isotope dilution is an analytical method where the concentration of an element in a sample can be measured from the known concentration of an element in a spike solution, and the ratios of two isotopes of the same element in the natural sample and the spike respectively. The amount of an element in the sample, n_{sam} , is given by:

$$n_{sam} = n_{spk} \frac{R_{spk} - R_{mix}\Sigma_i R_{isam}}{R_{mix} - R_{sam}\Sigma_i R_{ispk}} \quad (4)$$

where R is the ratio of two isotopes, and $\Sigma_i R_i$ is the sum of ratios of all isotopes to a reference isotope (e.g., 76; see also 77, 78). We use an isotope spike ‘cocktail’, doped with isotopes of Mg, Ti, and Ca found in lower abundance in natural samples (**Supplemental Fig. S5**). Isotope spikes are prepared from powders of spiked TiO₂, MgCO₂ and CaCO₂. The pure spike Mg and Ca carbonate powders are digested using HCl, and the Ti oxide using HNO₃+HCl+HF. Following the digest each spike solution is calibrated by measuring the relative concentration of Mg, Ca, and Ti isotopes on a Thermo Scientific Neptune Plus multicollector ICP-MS for ~48 hours. Estimate of the error on the spike determination are < 0.1 ‰ based on replicate analysis. Individual spike solutions are then used to make an isotope spike ‘cocktail’ solution containing Mg, Ca and Ti

spikes. The cocktail is 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 calibration curve method whereby standards of known concentration 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 both accuracy and precision of measured concentrations (**Fig. 3**; see also 79). In addition to an iCAP TQ ICP-MS used to run samples for this study, we ran standards on other ICP-MS models in order to test the data quality achieved by a variety of widely available instruments (a Perkin Elmer NexION 5000 Multi-Quadropole ICP-MS and a Thermo Scientific Element High Resolution Magnetic Sector ICP-MS). On the iCAP TQ ICP-MS, we were able to achieve average analytical error on standards of 0.75% for Ti, 1.16% for Mg, 1.29% for Ca, and 2.54% for Na (not using isotope dilution), using a conservative approach to calculate error (the standard deviation of measurements as a percentage of the mean). In individual runs we were able to achieve analytical error of less than 0.5% for Ti, Mg, and Ca. Our results show that our isotope dilution technique 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 mesocosm ERW experiments, which allow us to independently estimate ERW and CDR by measuring the concentration of reaction products in plant, soil exchangeable fraction and leachate solution pools (see 28, 30, 32, 45-49, 51, 54). Each mesocosm contained a single C4 cereal crop *Sorghum bicolor* plant (see 32) with two different fertilizer treatments (nitrogen-phosphorus-potassium, NPK, or manure), to which a basalt feedstock was added equivalent to an application rate of 5 kg m⁻² (50 t ha⁻¹) and mixed to a depth of 12cm (for a detailed description of mesocosm design and construction, substrate and feedstock preparation and characterization, plant varieties and growth conditions, and irrigation regime, see *Supporting Information*).

Leachate was collected from mesocosms at six discrete leachate events, accounting for the 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, and the plant material (comprising shoots, roots and seeds). Using a conventional approach focused on reaction products, we calculated elemental budgets for cations for each mesocosm from the dissolved or non-mineral-bound pools (leachate + soil exchangeable fraction + plant material) (see *Supporting Information Section 1.8*). We compared the elemental budgets calculated for basalt-amended mesocosms to 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. The excess Na⁺, Ca²⁺, and Mg²⁺ in the elemental budget of basalt-amended mesocosms relative to the controls were assumed to represent reaction products of basalt dissolution. From the amounts of these cations we obtained initial ERW

rates. Using a modified Steinhour formulation that relates the amount of mobile cations to the amount of carbonic acidity converted to bicarbonate (see *Supporting Information Section 1.3*), ERW rates were converted to CDR estimates.

These rates can be compared with those obtained using the TiCAT method, as the cations released into non-mineral-bound 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 12cm portion of each mesocosm. We calculated F_D of the basalt fraction present in the soil + basalt mixture separately for each major cation (see Section 2.1, also *Supporting Information Section 1.9*). From the cation F_D for each mesocosm and using the application rate of basalt for each mesocosm, we calculated the total amount of cation in feedstock applied over a given area that was dissolved (n^i ; see *Supporting Information Section 1.9*), giving an initial ERW rate, and using the same modified Steinhour formulation 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 (see *Supporting Information Section 1.10*).

3 Results and Discussion

Our results show agreement between two independent methods of calculating CDR in our mesocosm systems, with a systematic offset (**Fig. 4a**). The conventional approach, measuring cation reaction products in dissolved cation pools, yielded mean CDR estimates of 1.68 ± 0.22 tCO₂eq ha⁻¹ (NPK-fertilized) and 1.05 ± 0.38 tCO₂eq ha⁻¹ (manure-fertilized) across all mesocosms. The TiCAT approach introduced here, which measures cation loss from the solid phase of soil samples, gave mean CDR estimates of 1.96 ± 0.79 tCO₂eq ha⁻¹ (NPK-fertilized) and 0.97 ± 1.43 tCO₂eq ha⁻¹ (manure-fertilized). Thus, mean CDR estimates from these methods were within error (\pm standard error of means) for both NPK- and manure-fertilized basalt-amended mesocosms.

Mean initial CDR values across all basalt-amended mesocosms were 1.47 ± 1.09 tCO₂eq ha⁻¹ (TiCAT), and 1.36 ± 0.40 tCO₂eq ha⁻¹ (dissolved pools) (**Fig. 4b**). This is broadly consistent with estimated CDR values calculated for similar ERW studies, albeit these range greatly in application amount and duration (see 33). 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 235 days of carbonic-acid-driven weathering was 15.8 ± 11.6 % of this potential, using results from TiCAT. Analysis of total inorganic carbon (TIC) and ammonium acetate leaching strongly suggest that carbonate formation and exchangeable cations in basalt feedstock should have a negligible impact on the overall cation budget of the mesocosm systems (*Supporting Information*). 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.

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. 54, involves many months of labor- and time-intensive sampling not only of soils, plants, and possibly porewaters from the agricultural plots onto which ERW feedstock is applied, but also 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., 80); and sampling of drainage waters may be impossible in drier environments or intervals. Such measurements, as well as those reliant on directly measuring soil exchangeable cations, can also be complicated by varying timeframes over which cations are bound to exchangeable sorption sites within a soil (see 46, 47).

Our approach also directly overcomes possibly the largest uncertainty in scaling ERW within agricultural settings — estimating the initial extent of feedstock dissolution in soils (see e.g., 33; 56). There is currently significant uncertainty on 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 feedstock has the potential to alter mineral dissolution rates (e.g., 81-89). In addition, bulk mineral dissolution kinetics are in some cases poorly constrained (e.g., 85, 90, 91). 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 (33, 56, 81-91).

A significant additional advantage to 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., 92, 93). Importantly, this means that there is already extensive personnel and infrastructure in place that can be leveraged to scale empirical validation of carbon capture through 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 (e.g., the US Department of Agriculture's COMET-Farm calculator, see <http://www.comet-farm.com>), which does not allow for landowners and land users to include alkalinity generation through practices such as ERW into 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 combined use of ERW and SOC maintenance to achieve maximum carbon storage depending on local conditions.

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 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., 20, 58). In addition, a large fraction of the dissolved cation load in any soil will be transiently hosted in soil exchange sites (e.g., 93-96; see also 51). 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 46, 47). However, there is a time-varying lag between feedstock dissolution and CO₂ capture that needs to be considered for accurate CDR quantification. As a result, 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, 43) and river-ocean system (20) 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 net CDR rates.

There are several key challenges that need to be met before TiCAT can be widely applied. First of all, 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. Secondly, spatial heterogeneity of elemental concentrations in managed soils must be examined to assess the density of sampling that must be implemented to infer weathering rates at field-scale; in both cases, specific sampling protocols such as pooling and/or gridded sampling may be useful tools in making representative measurements (97). Additionally, the TiCAT approach may not be viable as an MRV framework on its own in specific cases: in settings with high physical erosion; in settings where there is significant and fast weathering from soils; or where feedstocks are used that do not contain measurable amounts of a reference immobile element.

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 ICP-MS measurements (see 74, 75). Nonetheless, here we have demonstrated that it is possible using isotope dilution on a standard quadrupole ICP-MS instrument to minimize analytical error to ~1%, making even <10% basalt dissolution analytically resolvable for total feedstock application rates of 50 t ha⁻¹. However, 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., 98).

4 Conclusion

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. TiCAT yields estimates that 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 that a dissolution signal is resolvable 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 to be used for MRV in 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 final CDR. Nevertheless, our results suggest that the TiCAT method could be a cost-effective and accurate centerpiece of a robust MRV toolkit for deploying ERW at scale.

Figures

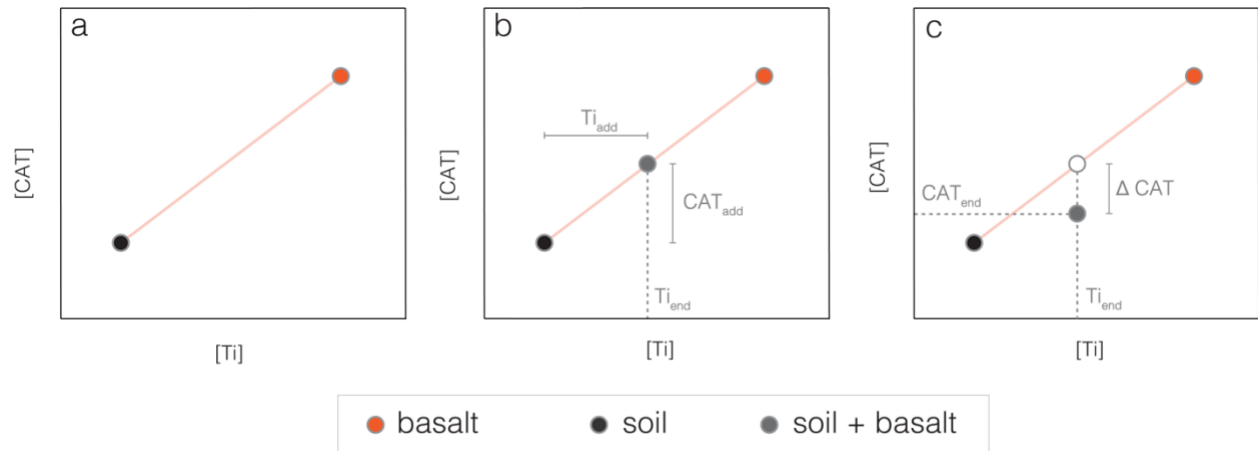


Fig. 1. The TiCAT conceptual framework as a simple two-component mixing model. An idealized soil and basalt endmember are plotted in Ti v CAT space (a). A mixture of soil + basalt initially plots on the idealized mixing line between both endmembers (b). Dissolution results in loss of CAT from the solid phase, while Ti is conserved as it 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 ΔCAT is the amount of CAT lost by dissolution (c).

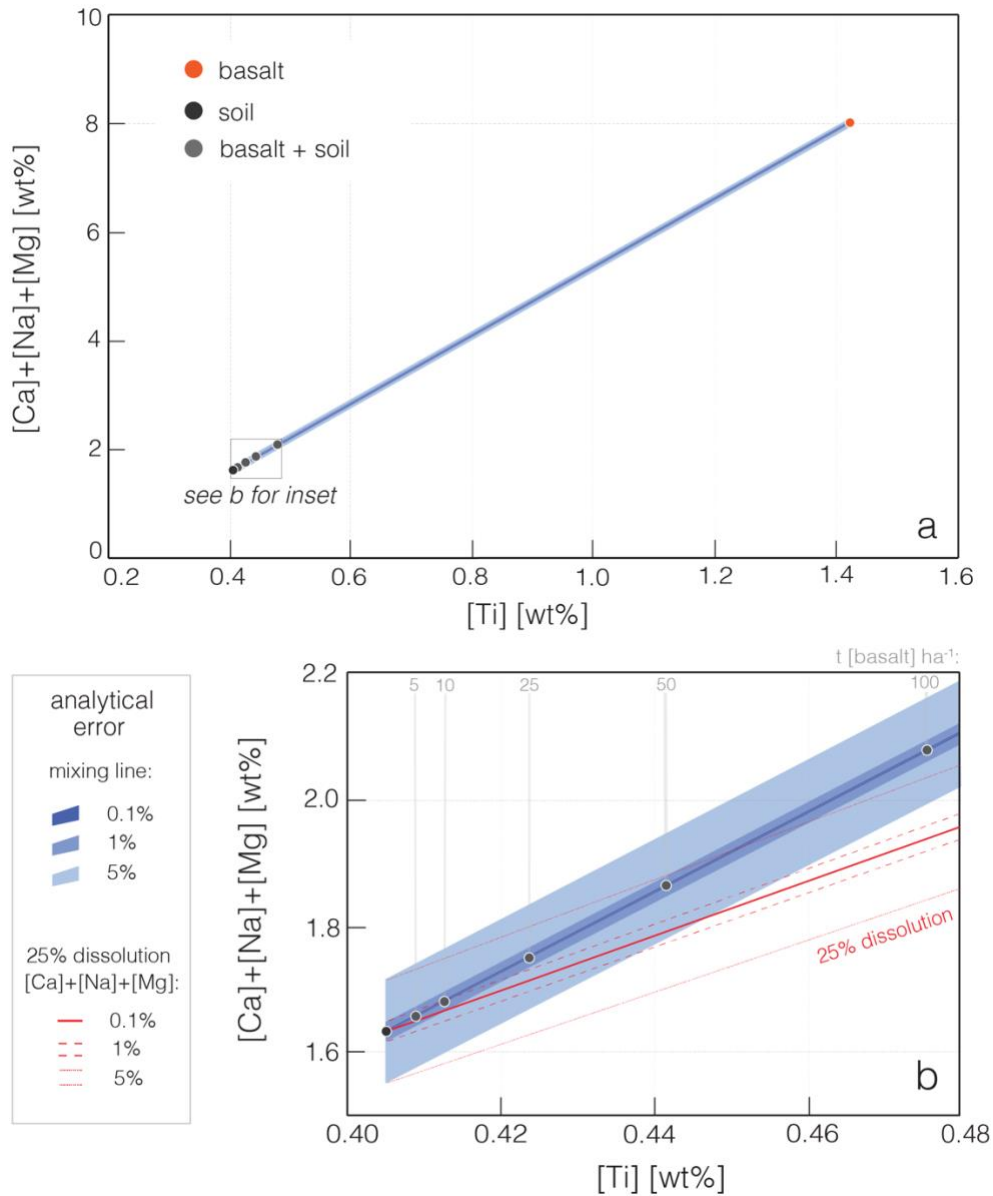


Fig. 2. A mixing model with representative data for soil and basalt endmembers. Assumed homogeneous mixtures of soil + basalt are shown for a range of basalt application scenarios (see inset, b). Error envelopes are shown for the mixing line and a line indicating theoretical 25% dissolution, based on potential size of analytical error on soil + basalt samples. Resolvability of a dissolution signal is dependent on dissolution rate, basalt application rate, and analytical error. Mixing line error envelope is given assumption that absolute analytical error of basalt is same as soil, a realistic scenario given repeat measurements of a bulk feedstock.

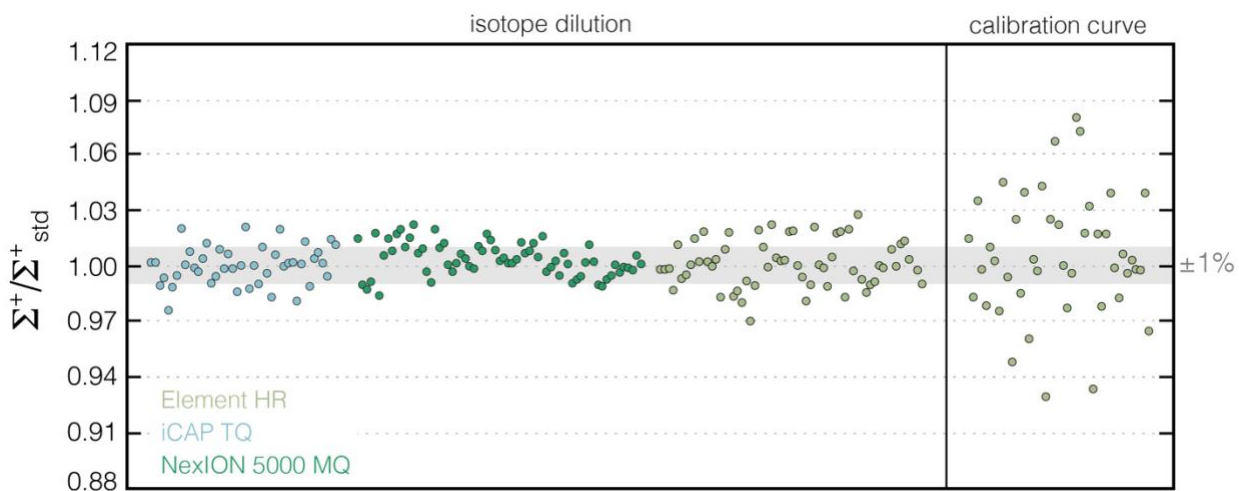


Fig 3. Representative analytical error for Ca, Mg, and Ti on standards run on three different ICP-MS instruments, using a calibration curve method and our isotope dilution method. Isotope dilution cannot be applied to Na as it has a single stable isotope. The grey shaded region represents an analytical error range of $\pm 1\%$. ICP-MS instruments used were two quadrupole instruments, a Thermo Scientific iCAP TQ ICP-MS and a Perkin Elmer NexION 5000 Multi-Quadropole ICP-MS; as well as a Thermo Scientific Element High Resolution Magnetic Sector ICP-MS.

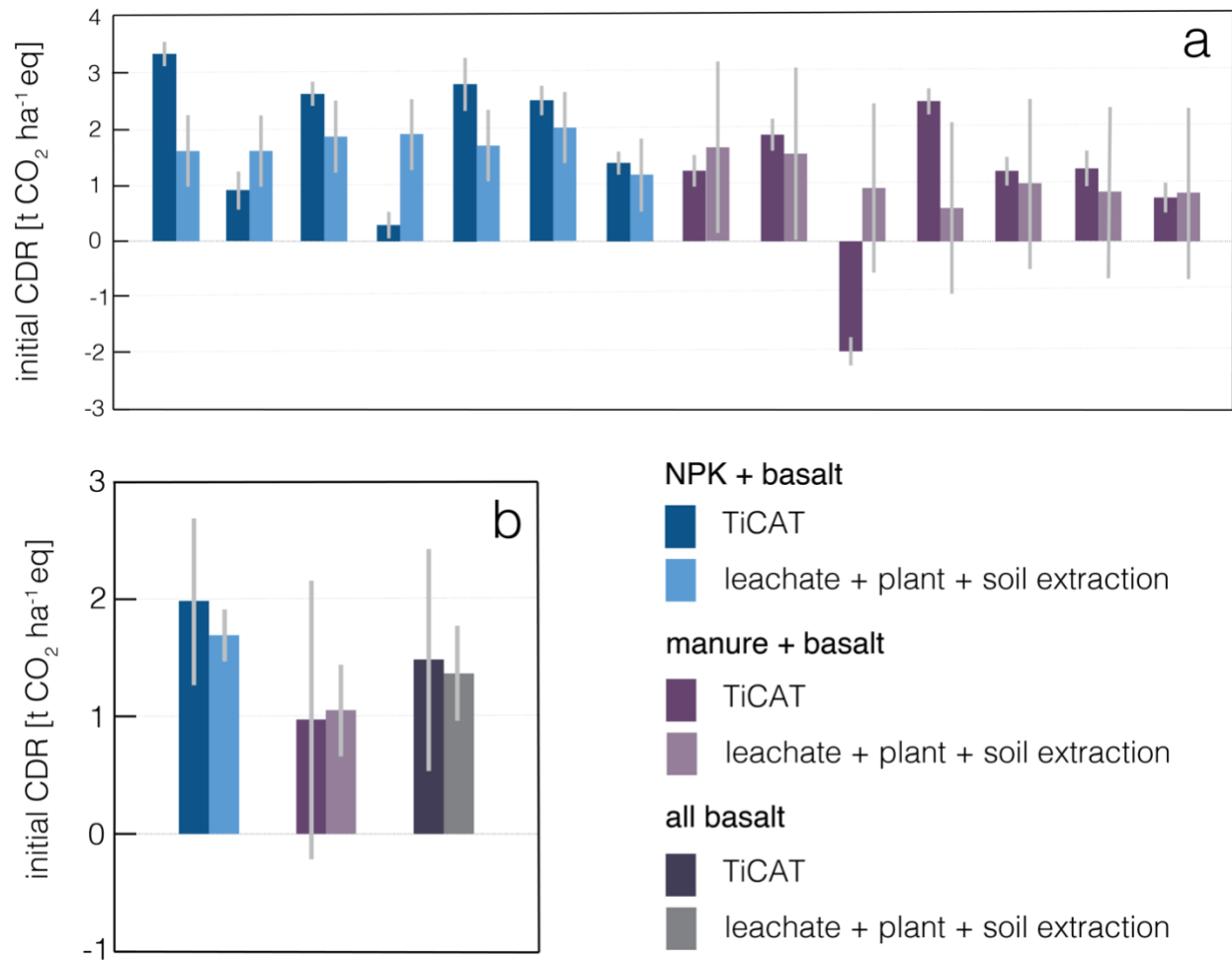


Fig 4. Initial CDR estimates calculated using cation data from TiCAT and from non-mineral-bound cation budgets. Results are shown for individual mesocosms (a), and as mean values for all mesocosms pooled by treatment type, where dark grey bars show all basalt-treated mesocosms as a single pooled data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

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