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LETTER

Direct evidence for atmospheric carbon dioxide removal via enhanced weathering in cropland soil

Iris O Holzer[1,*], **Mallika A Nocco**[1] and **Benjamin Z Houlton**[1,2]

[1] Department of Land, Air and Water Resources, University of California, Davis, Davis, California, 95616, United States of America
[2] Department of Ecology and Evolutionary Biology and Department of Global Development, Cornell University, Ithaca, New York, 14853, United States of America
[*] Author to whom any correspondence should be addressed.

E-mail: ioholzer@ucdavis.edu

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Abstract

Enhanced weathering of soil-applied crushed silicate rocks may remove substantial atmospheric carbon dioxide; however, field testing of this negative emission technology is lacking. Models have suggested that enhanced weathering could, in principle, remove billions of tons of CO_2 each year across global croplands, but methodological limitations have hindered direct measurement of CO_2 sequestration via crushed rock amendments in agriculture. Further questions remain concerning the efficacy of this technology in arid climates. Here we provide direct evidence of rapid CO_2 removal via enhanced weathering in soil pore water samples from a corn (*Zea mays* L.) cropping system in California. From December through February, during an extreme drought in our study region, we demonstrate a 2.6 to 2.9-fold increase in *in situ* bicarbonate alkalinity in response to additions of metabasalt and olivine fines. We provide a field analysis of carbon removal via silicate rock amendments and suggest enhanced weathering can remove carbon dioxide even under moisture-limited conditions.

Introduction

Enhanced silicate weathering has been widely suggested as a potential negative emission technology for global working lands [1–4], and a small number of field and greenhouse studies have revealed increases in inorganic carbon in response to silicate mineral additions [5–9]. Global models have pointed to the large-scale potential for enhanced weathering, including as a tool for meeting commitments under the Paris Agreement [10–13]. However, systematic testing of enhanced weathering in real-world field settings is hitherto lacking [14]. A key uncertainty concerns the efficacy of enhanced weathering under extreme conditions where moisture may limit capacity for carbon dioxide removal. Given that climate change impacts such as heatwaves and droughts are already widespread, knowledge of the robustness of enhanced weathering under extreme conditions is essential to understanding its future efficacy. Here we show that enhanced weathering maintains modest carbon dioxide (CO_2) removal in a multi-acre field trial under an extreme drought in California, one of the largest agricultural producers globally.

While soils or biomass typically offer short-term carbon storage over years to decades, the conversion of CO_2 to carbonate or bicarbonate offers a path for carbon storage over 'virtually geological time scales' [15, 16]. Because of the long residence times of (bi)carbonate in soils or water and the global availability of silicate minerals, enhanced weathering may yield effective and secure CO_2 drawdown [1, 4, 17]; however, accounting for this carbon presents challenges [18]. Since silicate weathering is often limited by available surface area, increased weathering is achievable through the widespread application of crushed silicate minerals in surface

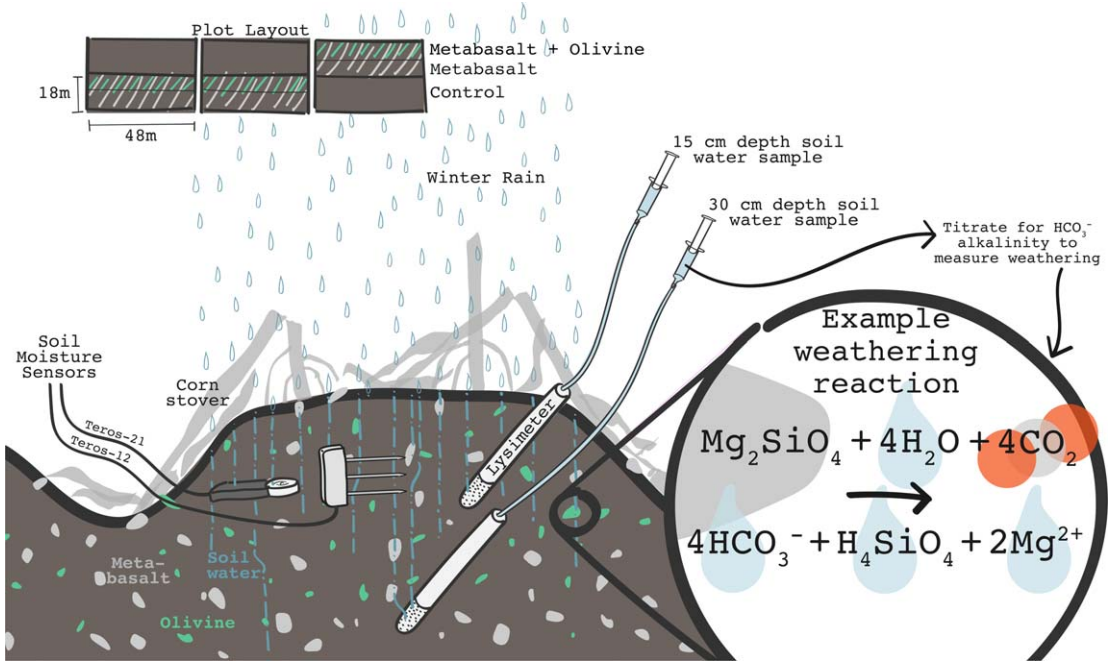

Figure 1. Experimental design and lysimeter installation locations. Lysimeters were installed at the depth of crushed rock incorporation (15 cm) and adjacent to the drip tape (30 cm). Image credit: Dr Bonnie McGill.

environments [19]. At present, a key uncertainty concerns enhanced weathering's effectiveness under conditions where moisture limitations constrain CO_2 removal. Recent modeling has suggested >2000 mm mean annual precipitation as the threshold above which CO_2 removal increases substantially due to greater weathering and leaching, though overall sequestration rates remain low [12]. If enhanced weathering is limited by moisture to this degree, its utility would fall exclusively in rainforests or highly irrigated environments. Given that 41% of earth's land surface is covered by drylands that are expanding due to climate change (~10% by 2100) [20], enhanced weathering in arid and semi-arid lands must be investigated.

Recognizing the paucity of field-based assessments, we tested the hypothesis that enhanced weathering is effective at removing CO_2 at multi-acre scales. While other soil amendments such as biochar or compost may add organic carbon directly to the soil, crushed rock that is devoid of carbonates but rich in silicates requires dissolution reactions for CO_2 removal. The initial evidentiary step of such reactions is the formation of bicarbonate, a dissolved form of inorganic carbon (figure 1). Since Ca- and Mg-silicate weathering initially yields dissolved bicarbonate across most terrestrial environments, we focused on pore water samplers (ceramic tension lysimeters) installed at two depths in 2020 in a five-acre field trial of corn in northern California. The observations reported in this replicated, controlled study span a short three-month interval during the fallow winter season (no irrigation or cover crop), the period of most precipitation in this xeric climate. Crushed metabasalt and olivine soil amendments were used to investigate changes in soil pore water alkalinity as a proxy for bicarbonate production. The metabasalt (median grain size: 102 ± 22 μm) was selected because of its benign elemental composition and modest weathering potential (the parent volcanics includes felsic facies, yielding an overall silica content in the intermediate-to-felsic range). The olivine (median grain size: 83 ± 12 μm), in contrast, was chosen for its potential to weather rapidly (figure 1; tables S2-S3).

Bicarbonate in soil pore water was selected as an indicator of CO_2 removal because it is produced from silicate minerals reacting with dissolved CO_2 during initial weathering [21] (figure 1). Subsequently, carbonate may precipitate in soils, or aqueous products including bicarbonate may leach to groundwater, surface waters, and eventually the ocean [1]. Carbonate or bicarbonate formation is controlled principally by soil pH and the soil's buffering capacity, and by the availability of reactants [21]. Given the surface pH of this system (6.95), early enhanced weathering is likely to be via bicarbonate production. When interpretating our results, we apply the assumption that alkalinity ≈ bicarbonate, given the circumneutral pH of the lysimeter solution that we analyzed by acidimetric titration [7, 22]. This assumption is robust because the pH of our samples never exceeds 7.6 or falls below 5.3 (mean = 6.8 ± 0.5), firmly in the zone of bicarbonate speciation (pH ~4.5–8.3). Future enhanced weathering work analyzing alkalinity in concert with other determinations of bicarbonate concentrations could help to confirm this expectation.

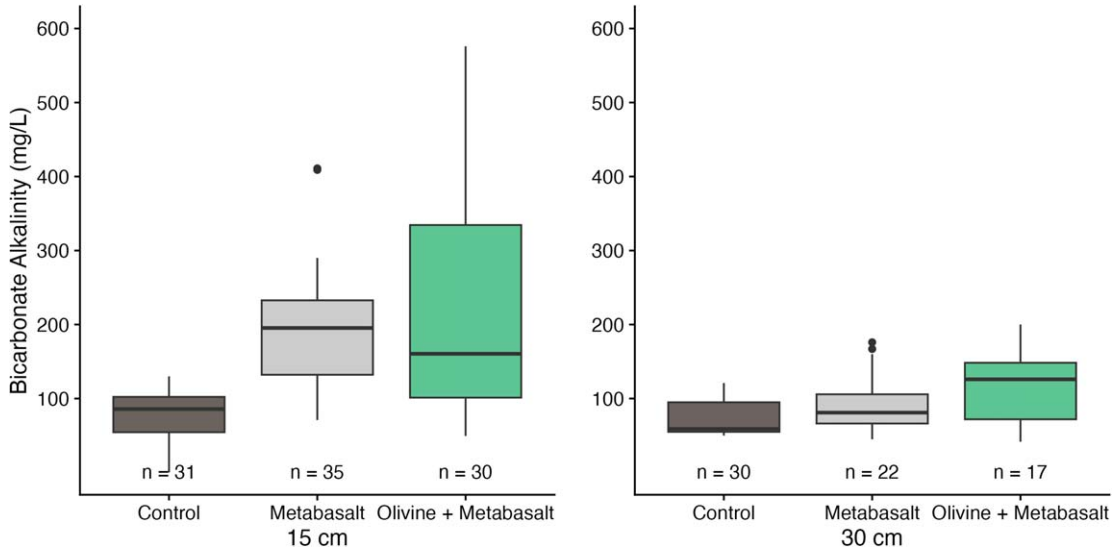

Figure 2. Composite dataset for winter 2020–2021 showing differences in bicarbonate alkalinity at 15 cm and 30 cm in control, metabasalt, and metabasalt + olivine amended plots. Data analysis was performed using $\log_{10}$-alkalinity; 'n' reflects collected number of samples. The boxes show the interquartile range, where the midline indicates median alkalinity. The whiskers indicate the minimum and maximum, with outliers shown as points.

Results and discussion

During an extreme drought period [23], with only 141 mm of winter precipitation from November 1, 2020 to March 1, 2021 (41% of the historical average), $\log_{10}$-bicarbonate alkalinity increased significantly in plots amended with metabasalt and olivine plus metabasalt (figures 2, 3(a)). This change was initially observed in December 2020 in the plow layer (15 cm) and later in February 2021 at depth (30 cm). The surge in alkalinity represents a 2.9-fold increase in olivine plus metabasalt amended plots and a 2.6-fold increase in metabasalt-only amended plots when compared to the unamended control at 15 cm depth (from an average of 74.4 mg l^{-1} to 219 mg l^{-1} and 190 mg l^{-1}, respectively; control versus olivine plus metabasalt $p < 0.0001$, control versus metabasalt $p < 0.0001$ for $\log_{10}$-alkalinity). This is consistent with the expectation that olivine weathers more quickly and generates more CO_2 removal than basalt.

At 30 cm depth, the increase was more modest, from 72.9 mg l^{-1} to 93.9 mg l^{-1} and 118 mg l^{-1}, respectively in control, metabasalt, and olivine plus metabasalt amended plots, a difference which was only significantly different for the olivine plus metabasalt amended plots versus the control (control versus olivine plus metabasalt $p = 0.008$; control versus metabasalt $p = 0.2$ for $\log_{10}$-alkalinity). However, this difference at 30 cm became more pronounced throughout the winter months, increasing from no initially observable differences to separation by treatment as the season progressed and water infiltrated deeper. Lengthier studies, many of which are in progress, are needed to assess if this difference represents a short, initial pulse of weathering to be followed by slower dissolution or if warmer temperatures and irrigation during the growing season will accelerate enhanced weathering. Moreover, because these lysimeters were not installed immediately following the initial rock application in 2019, we cannot state with certainty what fraction of weathering products may have been generated during the summer 2020 irrigation season. Since the field is subsurface drip irrigated below the level of rock incorporation, we expect most weathering to have occurred during the wet winter season.

The right-skewed nature of the bicarbonate alkalinity observations is due in part to spatial 'hot spots' observed in some of the olivine plus metabasalt treatment plots. This suggests potentially much higher rates of local weathering, perhaps due to unevenness in the application of crushed rock, which was administered by a mechanical spreader. Alternatively, preferential flow, differential microbial activity, non-systematic differences in mineralogy or rock particle size, or all of these, could affect the spatial distribution of bicarbonate observed in soil water. Assessing these mechanisms may help optimize future CO_2 removal. At present, this variation and associated uncertainty pose challenges for measurement, reporting, and verification of enhanced weathering carbon removal at large scales.

Given the 141 mm of winter rain and mean bicarbonate increases of 145 mg l^{-1} and 116 mg l^{-1} in the olivine plus metabasalt and metabasalt treatments relative to the control at 15 cm, we estimated carbon storage of 0.15 t CO_2 ha^{-1} and 0.12 t CO_2 ha^{-1}, respectively, during the study. While still relatively low, this carbon storage amount is higher than has been reported in recent modeling research [12], especially given the magnitude of

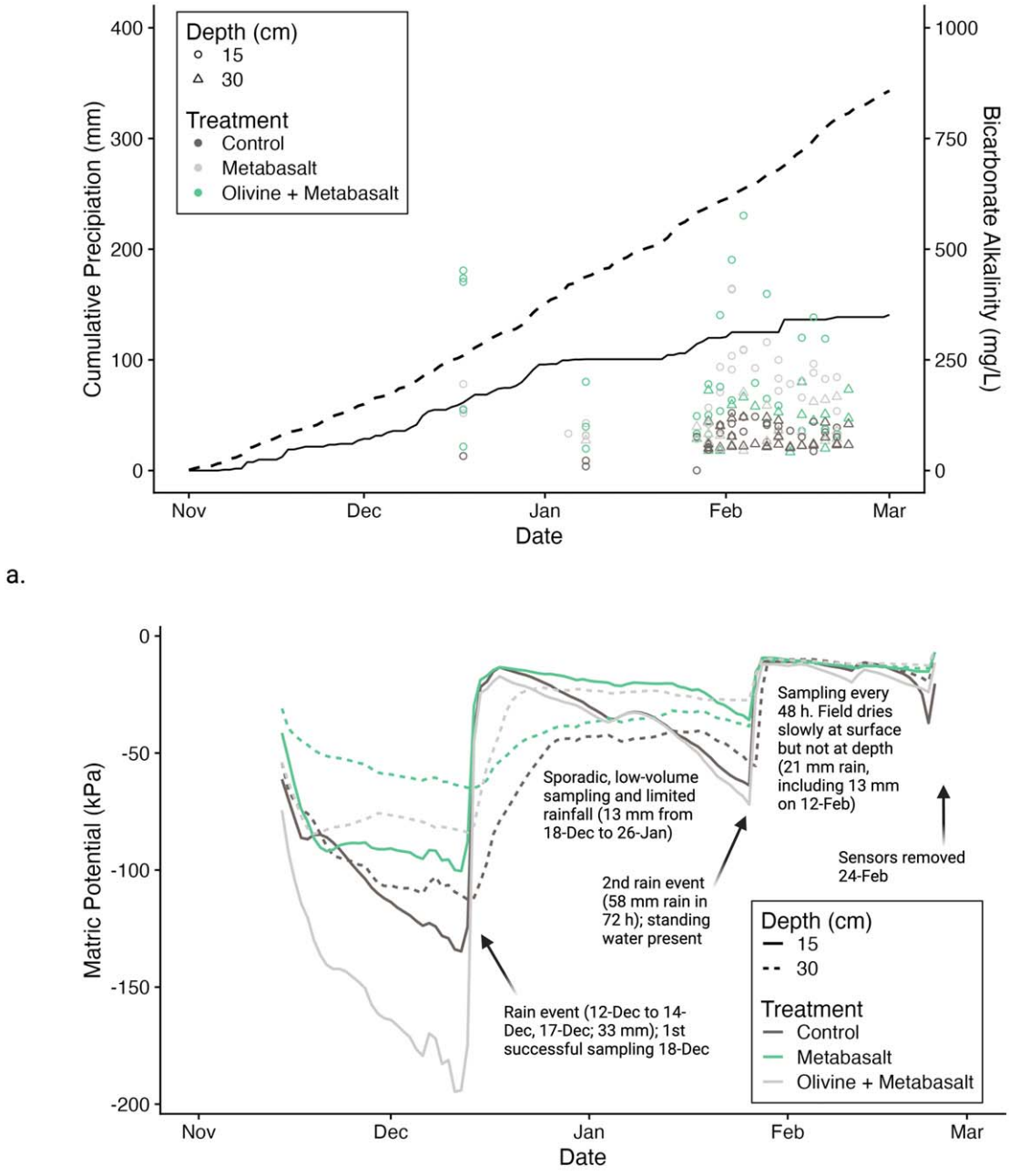

Figure 3. (a) Alkalinity by date, plus cumulative precipitation (mm), across the rainy winter months. The solid line shows cumulative precipitation at our site during the study period, while the dashed line shows historic cumulative precipitation for the same period from 1982–2022. (b) Soil matric potential (kPa) from Nov. 2020 to Feb. 2021, spanning the period of winter equipment installation. Key precipitation and sampling events are highlighted. Annotations created with BioRender.com.

precipitation. It is slightly higher than some previous soil core or greenhouse enhanced weathering estimates of 0.0102–0.049 t CO_2 ha^{-1} yr^{-1} [6, 24]. However, this number, like previous estimates, should be viewed with reasonable caution: it is based on relatively limited spatial coverage with lysimeters over only a few months. If we coarsely assume the theoretical maximum of 1.25 tons CO_2 removal per ton of forsterite olivine [6] applies to both the olivine and the non-quartz portion of the metabasalt, given the total rock application rate of 107.5 t ha^{-1} (43.5 t ac^{-1}), ~0.15% of maximum carbon storage has been achieved thus far for olivine plus metabasalt plots. Though this suggests substantial future weathering potential, present rates may represent a rapid, initial stage of dissolution to be followed by a much slower stoichiometric stage [25]. Future integration of detailed hydrologic measurements, as well as understanding rock amendment changes to soil hydrology, will improve flux-based quantification of enhanced weathering in the field, and longer trials will provide critical insight into stages of dissolution.

Although large-scale commercial enhanced weathering projects are moving forward, consensus is still lacking concerning best practices for projecting carbon dioxide removal, and the existing literature spans a limited number of soil types and climates. This active discourse is apparent in a recent critique of one group's carbon drawdown estimates in the United Kingdom [24, 26]. Therefore, our dataset, though small, represents a critical and timely contribution. Our findings support the hypothesis that enhanced weathering removes CO_2 in real-world settings, while simultaneously illustrating challenges in quantification under weather extremes. We find modest but direct evidence of CO_2 removal in this semi-arid cropland planted with corn, pushed to extreme aridity owing to historic drought [23], and at circumneutral soil pH. While humid, acidic environments encapsulate far greater enhanced weathering potential overall, this study in a Mediterranean climate during a historic drought suggests we may expand the margins of where enhanced weathering technology might operate into global arid lands.

Materials and methods

In November 2020, we installed lysimeters at a five-acre Davis, CA trial of irrigated corn (*Zea mays*) to investigate changes in soil pore water alkalinity from enhanced weathering. This site, located at the University of California, Davis and part of the Working Lands Innovation Center, is characterized by circumneutral soil pH and young soils (Xerofluvents) and lacked both irrigation and ground cover during the winter months (tables S1). This work focuses on a subset of treatments at this site, which was also amended with biochar and compost in a full-factorial randomized complete block design (figure S1).

Metabasalt, a mining byproduct, was applied at 40 t ha^{-1} in fall 2019 and fall 2020 (Specialty Granules LLC, Ione, CA), while olivine, also a mining byproduct, was applied at 27 t ha^{-1} in fall 2020 (via Rock Dust Local, Bridport, VT). Mineralogy of the olivine and metabasalt were determined using QEMSCAN Bulk Mineral Analysis (Bureau Veritas Mineral Laboratories), while grain size was measured using an LS-230 Particle Size Analyzer (tables S2-S3).

Ceramic tension lysimeters (Soilmoisture Equipment Corp. 1900L Near Surface Samplers), selected for their affordability and suitability for measuring carbonate species and pH [27], were placed at the depth of amendment incorporation (15 cm) and at the subsurface drip irrigation depth (30 cm). Lysimeters were installed in plots amended with metabasalt, metabasalt and olivine, and in unamended control plots (3 plots per treatment; 18 lysimeters total). They were paired with sensors measuring volumetric water content, temperature, and electrical conductivity (METER TEROS 12) and soil matric potential (METER TEROS 21), connected to METER ZL6 data loggers. Climate data for the study period were retrieved from three weather stations at the site (NCDC #2294; TouchTone #12; CIMIS #6) [28].

Lysimeters were vacuumed to −33 kPa; water samples were collected 24–72 h later using plastic syringes. Sporadic low-level sampling was achievable during dry periods, and frequent sampling occurred after heavy rain events (figure 3(b)). Still, total sample collection was severely inhibited by overall low rainfall. Samples were refrigerated at 4°C and titrated within ~48 h initially using a Hach Manual-Digital Titrator (16900) and 0.1600 N H_2SO_4 and later using a Hanna Instruments automatic potentiometric titrator with attached autosampler (HI902C/HI921) and 0.01 N HCl [28]. Alkalinity was calculated using a combination of end point, inflection point, and gran plot methods. We do not report dissolved organic carbon (typically a minor contributor to alkalinity), as ceramic lysimeters tend to preferentially sorb organic compounds, decreasing concentrations in soil solution [27].

Data analysis and visualization were performed using R statistical software (version 4.2.1), RStudio (version 2022.07.1+554), and the packages *cowplot*, *emmeans*, *lmtest*, and *lubridate*, as well as the *tidyverse* collection of packages [29–35]. Data were transformed on a $\log_{10}$-scale to reduce non-normality and heteroscedasticity. Linear models were fit to transformed data using the *lm* function, and these models were evaluated using ANOVA and Tukey's HSD pairwise-comparisons.

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Data availability statement

The data that [28] support the findings of this study will be openly available following an embargo at the following URL/DOI: https://doi.org/10.5281/zenodo.7668368. Data will be available from 16 October 2023.

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Author contributions

IOH designed and carried out the experiment and conducted data analysis with support from MAN and BZH. IOH wrote the manuscript with contributions from MAN and BZH. BZH conceived the original idea for the Working Lands Innovation Center and supervised the project.

Ethical statement

The crushed metabasalt was donated by Specialty Granules LLC, with shipping costs paid by the research group.

ORCID iDs

Iris O Holzer https://orcid.org/0000-0002-1293-7808
Mallika A Nocco https://orcid.org/0000-0002-6067-8759
Benjamin Z Houlton https://orcid.org/0000-0002-1414-0261

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