**Eion Corp Whitepaper** 

# Methodology for CO<sub>2</sub> Removal by Enhanced Mineralization on Croplands

Adam Wolf Princeton NJ

Alison Marklein Oakland CA

> Elliot Chang Oakland CA

Corresponding Author: elliot@eion.team

30<sup>th</sup> March, 2023



# Contents

1	Sources	3			
2	Summary Description of Methodology				
3	Definitions	4			
4	Applicability Conditions	5			
5	Project Boundary	6			
6	Baseline Scenario	7			
7	Additionality	7			
8	Quantification of GHG Emissions and Removals8.1Baseline Emissions8.2Project Emissions8.2.1Stage 1: Quarry8.2.2Stage 2: Transport Quarry to Mill8.2.3Stage 3: Mill8.2.4Stage 4: Transport Mill to Field8.2.5Stage 5: Field Application8.3Carbon Dioxide Removal8.3.1Potential CDR8.3.2Actual CDR8.4System Loss8.4.1River DRI8.4.3Global oceanic baseline DRI8.4.4Localised annual oceanic DRI8.4.5Soil DRI	7 8 8 10 11 11 12 12 14 20 20 21 21 21 22			
9	Monitoring9.1Data and Parameters Available at Validation9.2Data and Parameters Monitored	<b>23</b> 23 24			
Aŗ	Appendices 30				
A	Electricity Grid Emissions Factors30				
B	Transportation Emissions Factors 31				
C	2 Determination of crop lime requirement 32				
D	Derivation of DRI         D.0.1       Aqueous Carbonate System Chemistry	<b>33</b> 39			

# **List of Figures**

5

6 7

8

A1

A2

A3

1	Chemical transformations in carbon capture by enhanced mineralization on croplands.	3
2	Project Boundary for Enhanced Rock Weathering Life Cycle.	6
3	DIC Uptake Index, showing ideal range for soil uptake.	13
4	Simplified budget equation of divalent cations that remove $CO_2$	16
5	US River water samples: DRI vs. pH	21
6	Localised mean oceanic DRI for years 1958 - 2018, at 1 x 1 degree resolution	22
7	DIC speciation vs. pH, showing $CO_2$ , $HCO_3^-$ , and $CO_3^{2-}$ , on a log scale (left) and as a	
	fraction of total DIC (right)	34
8	Carbonate species as they comprise DIC (left) and total alkalinity (right) across a	
	range of pH.	36
9	Change in derivatives of carbonate system with respect to changes induced by a	
	change in alkalinity. Derivatives of DIC (left) and pH (right).	38
10	This figure shows carbonate alkalinity vs. pH. The dashed lines show where pH=8.3,	
	and carbonate alkalinity = -2.5.	40
11	Changes in DIC and TA driven by pH.	41
12	Changes in dDIC/dTA and dpH/dTA driven by pH	42
Listo	of Tables	
	i iables	
1	Boundary Table	7
2	River DRI Input Sources	21
3	Global Ocean DRI Parameter Values	21
4	Soil DRI Parameters	22

Data and Parameters available at validation: Carbon Dioxide Removals . . . . . . . 24

Calcium Carbonate Equivalent of silicates in references to common aglimes. . . . . . 33

23

25

# 1 Sources

This methodology is informed by the following methodologies:

- VCS methodology VM0043, Methodology for CO<sub>2</sub> Utilization in Concrete Production.
- 40 CFR Part 98, Subpart RR, Geologic Sequestration of Carbon Dioxide
- 40 CFR Part 98, Subpart HH, Municipal Solid Waste in Landfills

# 2 Summary Description of Methodology

Enhanced mineralization (EM) is an approach to carbon dioxide capture recognized by the Department of Energy that results in the permanent sequestration of  $CO_2$  as dissolved inorganic carbon (DIC) (Figure 1). On croplands, defined by the USDA as including cultivated crops, pastures, rangelands and managed woodlands, the carbon captured by EM originates largely as respiration within the pore space of soils. In this soil pore space, the  $CO_2$  concentration is greatly elevated compared to the atmosphere, which accelerates the process. In this context, the process is commonly called enhanced rock weathering (ERW), because it mimics the natural process by which rocks weather into secondary minerals, resulting in a flux of cations and DIC into the ocean. The weathering process is thermodynamically irreversible, and results in the permanent storage of DIC in saline marine environments with a lifetime of carbon on the order of 500,000 years. Inventories of appropriate minerals suggests that the potential scale of carbon removal is ~35,000 Gt of  $CO_2$  (~500 years of current global emissions) [1]. Recent studies focused narrowly on land application of silicates suggests the US, China, and India could each be capable of 0.5Gt  $CO_2$  removal per year [2].

Figure 1: Chemical transformations in carbon capture by enhanced mineralization on croplands.



The key processes in ERW include:

- 1. Extraction of minerals from a quarry, including primary crushing activities
- 2. Transportation from the quarry to a processing facility ("mill")
- 3. Processing of minerals to a fine particle size with high surface area (>1m2/g) that represents a sensitized sorbent with high reactivity for CO<sub>2</sub> removal
- 4. Transportation from the mill to a field
- 5. Application of the mineral sorbent onto the field
- 6. The carbon capture, utilization, and sequestration process of mineral weathering in soils (CCUS)

7. Downstream transport of captured carbon from the field to the ocean

Among these seven distinct stages, the first five emit  $CO_2$  as industrial processes. These processes demand energy from the grid (as a mill) or fuel (for transportation), and as such are readily accounted for by conventional lifecycle analyses (NETL cite or 40CFR Part 98 cite) that utilize direct measurements to account for their greenhouse gas emissions. These processes may also have one time capital expenditures, for example for equipment manufactured from steel, or facilities that use concrete, which is also accounted for using conventional methodologies.

The sixth step, the CCUS step in the weathering process, has been the limiting factor for ERW to be accounted for in carbon accounting, because methodologies have either been developed for quantifying (a) weathering rates in the solid phase, or (b) weathering rates at basin or watershed scales, but never at the individual field scale. The present methodology largely focuses on this step.

The final step is analogous to the estimation of leakage of  $CO_2$  from subsurface reservoirs from carbon captured and injected from point sources. The system loss within monitoring areas in the United States can be evaluated by using historical data from federal sources (e.g. USGS) with models developed at National Labs. Subsequent to project implementation, current data may be monitored to evaluate whether conditions exist for actual system losses exceeding anticipated losses. Other data may exist for regions outside of the United States.

## 3 Definitions

#### Aglime

Calcite  $(CaCO_3)$  or dolomite  $((CaCO_3)(MgCO_3))$ , generally with a high concentration of Ca and/or Mg, and with a particle size distribution meeting agricultural requirements to be readily dissolved over 2-4 year time horizon. Aglime is generally a waste product from limestone extraction for the building and transportation industries.

#### Alkalinity

The charge balance of proton acceptors (which include carbonate species) over proton donors OR the charge balance of cations (which include calcium and magnesium) over anions. These two expressions are by definition equal, and sum to zero net charge of a solution.

#### **Carbonate System**

The pH-dependent speciation of  $H_2CO_3$ ,  $HCO_3^-$ , and  $CO_3^{2-}$ . The carbonate system parameters that define the equilibrium between these species is determined by temperature and salinity.

#### Cropland

Cultivated annual and perennial crops, pastures, rangelands and managed woodlands.

#### DIC

Dissolved Inorganic Carbon, consisting of  $H_2CO_3 + HCO_3^{-} + CO_3^{2-}$ .

#### **Enhanced Mineralization**

Mineralization of  $CO_2$  is a process that reacts alkaline material with  $CO_2$  to form solid carbonate minerals, for  $CO_2$  removal from air, for stable and permanent carbon storage, or for post-processing, where the alkaline agents are separated, and the  $CO_2$  is stored elsewhere. Sources of alkalinity (i.e., Mg- and Ca-rich silicate materials) can be naturally occurring minerals (such as olivine) or waste material from industry or quarry operations.

#### Leakage

In the context of ERW, leakage is the loss of captured  $CO_2$  to the atmosphere due to a change in the

carbonate system, due to changes in pH, salinity, or temperature.

#### LCA

Life Cycle Analysis, meeting ISO 14040 and 14044 standards, and optionally meeting additional DOE NETL CO2U requirements.

#### **Mineral Trapping**

Mineral trapping refers to a reaction that can occur when the Ca and  $HCO_3^-$  dissolved in alkaline water is precipitated inorganically or calcified by aquatic organisms into calcite. In marine environments, the calcite may be deposited at the bottom of the ocean, where it persists for millenia. In these settings, the calcium may be substituted by magnesium, forming dolomite.

#### **Solubility Trapping**

In solubility trapping, captured  $CO_2$  will dissolve into alkaline water that is present in soils, freshwater, and marine waters. At the  $CO_2$ /water interface, some of the  $CO_2$  molecules dissolve into the alkaline water within the soil's pore space. When  $CO_2$  dissolves in water it forms a weak carbonic acid ( $H_2CO_3$ ) and eventually bicarbonate ( $HCO_3^-$ ).

# 4 Applicability Conditions

This methodology is globally applicable to project activities that include ERW applied to croplands to remove  $CO_2$  from the atmosphere. The applicability conditions are built around some basic principles, namely that the project genuinely removes  $CO_2$ ; that this removal is empirically verifiable; that the project does not cause harm; and the project conforms to applicable law. There is a bias towards projects that are in mildly acidic to neutral croplands where carbon is maintained in the liquid phase and flows into the ocean; little consideration is given towards projects that result in accumulation of solid carbonates.

Project activities must meet the following conditions:

- The emissions from the project activity itself must not exceed its life cycle emissions. The system boundaries for accounting the carbon footprint of the project must include five process stages: extraction, transport, processing, application, and capture/sequestration.
- The silicate mineral used for this project shall have sufficient concentration of alkaline elements (Ca, and Mg) to exceed potential crop uptake, and result in capture of dissolved CO<sub>2</sub>.
- The soil type of the system shall be considered. Soil pH should range from 5.5 7.5. Sites with histic epipedons such as peat bogs, mangrove swamps, should be avoided until more information on their full greenhouse gas budgets are available.
- The land use type shall be considered. For example, pristine rainforests should be avoided until more information is available.
- The geography of the applied material shall be considered to account for the fate of captured carbon and cations: (a) into marine environments, (b) into acidic lakes, (c) into alkaline lakes (or evaporated). These settings determine the magnitude of leakage.
- The agronomic application of minerals shall not lead to a reduction in plant productivity, which would lead to expansion of crop production elsewhere, creating leakage.
- The project developer shall have agreements from the land owner or manager that transfer title of carbon removals to the project developer. These agreements shall be made available to an independent verifier.
- This methodology may apply to products that are not primary minerals coming from a surface quarry; however the additional safety considerations of such feedstocks are outside of the scope of this methodology.

# 5 Project Boundary

As illustrated in Figure 2, the spatial extent of the project boundary encompasses all of the stages identified in Section 2, which are analyzed in the Eion Whitepaper "Life Cycle Analysis and Full Carbon Accounting of Enhanced Rock Weathering".

These stages include:

- 1. The quarry where the product is extracted
- 2. Transportation from the quarry to the mill
- 3. The mill where the product is pulverized to an appropriate particle size
- 4. Transportation from the mill to the field
- 5. Application on the field
- 6. Chemical transformations within the field resulting in carbon capture and sequestration
- 7. Hydrologic transport of cations and DIC to its ultimate sink, with attendant system losses.



Figure 2: Project Boundary for Enhanced Rock Weathering Life Cycle.

To the extent that emissions factors for fuel and grid power account for non-CO<sub>2</sub> greenhouse gases, then these are included in the LCA; however in Stages 6-7 other GHGs are ignored. Note however that there is evidence that  $N_2O$  emissions are reduced with application of alkaline silicates in agricultural settings [3].

	Gas	Included?	Explanation
Material Source	CO <sub>2</sub>	Yes	Equipment and power usage
	CH <sub>4</sub>	No	Excluded for simplicity, emissions are negligible
	N <sub>2</sub> O	No	Excluded for simplicity, emissions are negligible
	Other	N/A	Other GHGs are not involved
Material Transport	CO <sub>2</sub>	Yes	Equipment and power usage

	CH <sub>4</sub>	No	Excluded for simplicity, emissions are negligible
	N <sub>2</sub> O	No	Excluded for simplicity, emissions are negligible
	Other	N/A	Other GHGs are not involved
Cropland application	CO <sub>2</sub>	Yes	Equipment and power usage
	CH <sub>4</sub>	No	Excluded for simplicity, emissions are negligible
	N <sub>2</sub> O	No	Excluded for simplicity, emissions are negligible
	Other	N/A	Other GHGs are not involved
In-situ removal	CO <sub>2</sub>	Yes	Primary removal mechanism
	CH <sub>4</sub>	No	Not involved
	N <sub>2</sub> O	No	Not involved
	Other	N/A	Other GHGs are not involved
Hydrologic transport	CO <sub>2</sub>	Yes	Natural release at ocean interface
	CH <sub>4</sub>	No	Not involved
	N <sub>2</sub> O	No	Not involved
	Other	N/A	Other GHGs are not involved

Table 1: Boundary Table

# 6 Baseline Scenario

The baseline scenario is the level of emissions that would take place in the absence of the project activity. In this case, it can be assumed that in the absence of the project, the  $CO_2$  removed by the activity would have remained in the atmosphere.

The alternate management on the soil would be to have lime application or no pH adjusting applications. Lime is neutral to negative  $CO_2$  sink, so assuming a 0 baseline is a conservative estimate.

The alternate use of the rock would be to remain in the mountain form, where the surface area of the rock is too small to weather at any meaningful rate; thus, no CO2 would be removed in the absence of the activity.

# 7 Additionality

The application of silicate minerals onto agricultural lands is rare, except in cases where silica is applied for silicon-demanding crops, such as sugarcane. Even so, soluble silica is generally low in the alkaline feedstocks that are needed for carbon capture. As such, application of silicate is considered *de facto* additional unless there is evidence that there is a history of alkaline silicate mineral applications at the site. In addition, the application of these minerals specifically for the purpose of  $CO_2$  removal is not taking place on any meaningful level. ERW as a CDR strategy is a brand new concept with nothing but a few pilot projects underway. The penetration rate of this project as a percentage of total farmland in the US or any other country is essentially zero.

# 8 Quantification of GHG Emissions and Removals

For a given year (y), net Carbon Dioxide removal  $(CDR_{net,y})$  is calculated as the actual CO<sub>2</sub> removed  $(CDR_{actual,y})$  minus project emissions  $(PE_y)$  minus the leakage fraction  $(LF_y)$ , according to the following equation:

$$CDR_{net,y} = CDR_{actual,y} - PE_y - LF_y \tag{1}$$

The project stages were outlined in Section 2 (Summary) and Section 5 (Boundary). Emissions are represented by Stages 1-5 (Section 8.2); carbon removal in Stage 6 (Section 8.3) and leakage in Stage 7 (Section 8.4). Baseline emissions for computing emission reductions is considered in Section 8.1, and accounts for each of these stages under the narrow case of silicate replacing aglime application. In general, the calculations are normalized to a single metric tonne of ore, which may then be integrated to the many tonnes of ore used in the project. This ore may be extracted on different days from the same quarry, follow different transport routes to individual fields, but otherwise have a constant elemental makeup and particle size.

#### 8.1 Baseline Emissions

Baseline emissions are assumed to be 0.

#### 8.2 Project Emissions

Project emissions account for the use of fuel and electricity in the extraction, transport, processing, and field application in Stages 1-5 of the process flow.

Project emissions in year *y* of the project crediting period will be expressed as follows:

$$PE_{y} = f_{Q} \cdot PE_{Q,y} + PE_{TQ2M,y} + PE_{M,y} + PE_{TM2F,y} + PE_{FA,y}$$
(2)

where:

$PE_y$	= Project emissions in year y (t $CO_2e$ )
$PE_{Q,y}$	= Total quarry emissions in year y (t $CO_2e$ )
$f_Q$	= Fraction of quarry activities involved in project (unitless)
$PE_{TQ2M,y}$	= Transport emissions from the quarry to mill in year y (tCO <sub>2</sub> e)
$PE_{M,y}$	= Mill emissions year y (t $CO_2e$ )
PE <sub>TM2F,y</sub>	= Transport emissions from the mill to field in year y (tCO <sub>2</sub> e)
$PE_{M,y}$	= Field application emissions in year y (t $CO_2e$ )

#### 8.2.1 Stage 1: Quarry

Quarry emissions are calculated as follows:

$$PE_{Q,y} = \left( V_{grid,Q,y} \cdot EF_{grid,Q} + \sum_{i} V_{fuel,i,y} \cdot EF_{fuel,i,Q} \right)$$
(3)

where:

$PE_{Q,y}$	= Project emissions from the quarry in year y (tCO <sub>2</sub> e).
$V_{grid,Q,y}$	= Quantity of electricity from the grid used by the quarry in year y(MWh).
$EF_{grid,Q}$	= Emissions factor of the electricity used to power the quarry ( $tCO_2e/MWh$ ).

V <sub>fuel,i,Q,y</sub>	= Quantity of fossil fuel of type <i>i</i> used by the equipment in the quarry in year y (unit of fuel, e.g. L).
EF <sub>fuel,i,Q</sub>	= Emissions factor of the fossil fuel of type $i$ used by the equipment in the quarry (tCO <sub>2</sub> e/unit of fuel).

**Determining**  $PE_{Q,y}$ : A life cycle analysis may be available for the quarry as a whole, or each product coming from the quarry, which assigns a summary emission factor for the feedstock (tCO<sub>2</sub>e/tOre). This avoids the need to determine  $V_{grid,Q,y}$  or  $V_{fuel,i,Q,y}$ . Under certain circumstances, the emissions of the feedstock may be zero if, for example, the emissions have been accounted for in other products coming from the quarry.

**Determining**  $V_{grid,Q,y}$ : The quantity of electricity from the grid used by the quarry in year y shall be determined using one of the following options:

#### **Option 1**: Electricity usage records.

**Option 2**: A bottom-up engineering model, such as Sherpa [4], which has been used to estimate emission in the US aggregate and limestone industry [5]. Applied generically, such a model may deviate by 20% or more from actual (per expert consensus in the industry) but can reach errors <5% if it is constrained by site-specific parameters. Site specific parameters that constitute a large fraction of the electricity profile include the size and duty cycle of crushers used in primary size reduction, alongside lighting, water pumps, conveyors, and facility electricity needs.

**Option 3**: Industry norms, such as may be drawn from cross-sectional surveys of enterprises with comparable mineral processing flows. This approach was taken to estimate costs of processing steps in [6].

**Determining**  $EF_{grid,Q}$ : Project proponents shall follow one of two alternatives to calculate this parameter:

**Option 1**: Use a grid emission factor published by a government agency. For example, for projects located in the United States use the eGrid emissions factor for the sub-region where the facility is located (latest available information). Where grid emission factors are not available from a government agency, an emission factor published by another reputable and recognized source, and reviewed for publication by an appropriated qualified, independent organization or appropriate peer review group, may be used (if available).

**Option 2**: Use the CDM Tool to calculate the emission factor for an electricity system.

**Determining**  $V_{fuel,i,Q,y}$ : The quantity of fossil fuel of type *i* used by the quarry in year y shall be determined using one of the following options:

#### **Option 1**: Fuel consumption records.

**Option 2**: As previously referenced for electricity, a bottom up engineering model constrained by site-specific information. Site specific parameters that comprise a large fraction of fuel usage includes Site specific parameters include the number and size of various pieces of equipment, distances traveled, and total ore production.

**Option 3**: As previously referenced for electricity, cross-sectional data can be used to provide a coarse estimate of fuel usage as a function of total ore production.

**Determining**  $EF_{fuel,i,Q}$ : Project proponents shall use a fuel emission factor published by a government agency.

#### 8.2.2 Stage 2: Transport Quarry to Mill

Milling involves final comminution (pulverizing) of the mineral feedstock from a top size of 6mm- to a final particle size D50 of  $\sim 100\mu$ m, subsequent to primary and secondary crushing and screening at the quarry. Quarries may or may not have such a facility on-site, which requires transportation to a mill for subsequent processing by a toller to reach the target particle size and agglomeration appropriate for field application and ERW. Thus, transportation may or may not be relevant to the project emissions budget.

Total project emissions for this transportation stage are calculated as:

$$PE_{TQ2M,y} = \sum_{i} PE_{TQ2M,j,y}$$
(4)

where:

$PE_{TQ2M,y}$	= Total transport emissions from the quarry to mill in year y ( $tCO_2e$ ).
$\sum_j$	= Summation over all transport legs $j$ .
PE <sub>TQ2M,j,y</sub>	= Transport emissions from leg $j$ from the quarry to mill in year y (tCO <sub>2</sub> e).

Calculation of  $PE_{TQ2M,j,y}$  for each transport leg *j* in year y can be achieved in two ways:

**Option 1**: Actual Fuel Usage. This is preferred when there is uncertainty as to which emissions factor to used, which varies considerably on the vehicle size and load (Appendix B). This is also relevant where the amount of ore moved is large, e.g. on a cargo vessel.

$$PE_{TQ2M,j,y} = \sum_{i} V_{i,j,y} \cdot EF_{i,j}$$
(5)

where:

$PE_{TQ2M,j,y}$	= Transport emissions from leg $j$ from the quarry to mill in year y (tCO <sub>2</sub> e).
$\sum_{i,j}$	= Summation over all fuel types $i$ used in leg $j$ .
$V_{i,j,y}$	= Quantity of fossil fuel of type $i$ used in leg $j$ in year y (unit of fuel, e.g. L).
EF <sub>i,j</sub>	= Emissions factor of the fossil fuel of type <i>i</i> used in transport leg <i>j</i> (tCO <sub>2</sub> e/unit of fuel).

**Option 2**: Transport Emissions Factor.

$$PE_{TQ2M,j,y} = D_j \cdot EF_j \tag{6}$$

where:

$PE_{TQ2M,j,y}$	= Transport emissions from leg <i>j</i> from the quarry to mill in year y (tCO <sub>2</sub> e).
$D_j$	= Distance in transport leg <i>j</i> .
EFj	= Transport emissions factor of conveyance used for transport leg $j$ .

Estimation of of  $D_j$  for each transport leg j can be achieved in two ways:

**Option 2**: GPS tracking of the vehicle, such as the AIS ship/barge tracking system or rail locator systems . This is particularly relevant when there is uncertainty as to the route taken, and is helpful in assessing proof of origin of a mineral.

**Option 2**: Automated route calculations for the vehicle, such as the Google Directions API or Bing Maps Directions API. This is more appropriate for short-haul truck deliveries, for which GPS tracking may be impractical or inaccurate and the emissions impact of deviations from the idealized route is low.

#### 8.2.3 Stage 3: Mill

Mill emissions are calculated as follows:

$$PE_{M,y} = V_{grid,M,y} \cdot EF_{grid,M} + \sum_{i} V_{fuel,i,M,y} \cdot EF_{fuel,i,M}$$
(7)

Definitions for these parameters, and guidance for estimating their values, are directly analogous to those for the quarry. More details on the drivers for these emissions, including the energy used for particle size reduction, can be found in the accompanying life cycle analysis.

#### 8.2.4 Stage 4: Transport Mill to Field

Transportation emissions from the mill to the field are calculated as follows:

$$PE_{TM2F,y} = \sum_{i} PE_{TM2F,j,y}$$
(8)

Definitions for these parameters, and guidance for estimating their values, are directly analogous to those for transport from the mill to the field.

#### 8.2.5 Stage 5: Field Application

Field Application is generally by a 50HP lime spreader with high flotation tires moving at constant speed across the field.

(9)

$$PE_{FA,y} = FPT \cdot TPMPA \cdot EF_i$$

where:

$PE_{TA,y}$	= Field application emissions (t $CO_2e$ ).
FPT	= Fuel usage per unit time (e.g. liters/hour). A 50HP motor uses approximately 5.87 L/H.
ТРМРА	= Application time per mass of mineral applied per area (e.g. hours/-tOre/acre). A 50 HP spreader can apply 2 tons per acre in 5 minutes.
$EF_i$	= Emissions factor of the fossil fuel <i>i</i> used for field application (kgCO <sub>2</sub> e/L).

*FPT* can be determined by conventional engineering calculations, e.g. a 50HP motor uses approximately 5.87 L/H. If available, an actual fuel survey is preferred.

*TPMPA* can be determined by conventional engineering calculations, else an as-applied map can be used to determine the total time spent, the total area covered divided, and the total mass of mineral applied.

 $EF_i$  can be determined as above for transportation emissions.

#### 8.3 Carbon Dioxide Removal

The process of silicate rock weathering is well understood, but the impacts of enhancement on the kinetic rates of the process are subject to uncertainty. The enhancement is achieved by first increasing in surface area of minerals through pulverizing the minerals, and subsequently adding these minerals to environments with elevated  $CO_2$ , acidity, moisture, and temperature. In agricultural systems these conditions can be quite dynamic, owing to plant growth, microbiological activity, and weather impacts on soil moisture and temperature regimes. Furthermore, there are spatial variations in soil physical properties (mineralogy, texture) and human management (application of fertilizer and other inputs). The following methodology is designed to constrain by direct measurement those elements of the system that are most variable (such as weathering rate), and to use the existing supply chain infrastructure to provide useful boundary conditions (e.g. amount delivered to the field and applied) wherever possible. An accompanying Project Design Document shall provide a theoretical rationale and empirical evidence for a Project Developer's approach to verifiability.

#### 8.3.1 Potential CDR

Potential CO<sub>2</sub> removal shall be estimated as :

$$CDR_{potential} = A \cdot AR \cdot \frac{1}{tOre} \cdot MP \cdot DUI$$
(10)

where:

CDR <sub>potential</sub>	= Maximum potential $CO_2$ removal ( $tCO_2/tOre$ ).
Α	= Area of mineral application (ha).
AR	= Application rate of mineral (tOre/ha).
tOre	= Total metric tons of mineral applied over area A (tOre).
MP	= Mineral potential of the applied silicate ( $tCO_2/tOre$ ).
DUI	= DIC Uptake Index of the soil, equivalent to $\frac{dDIC}{dAlk}$ , the moles of DIC taken up by soil solution per marginal unit of added alkalinity.

Figure 3: DIC Uptake Index, showing ideal range for soil uptake.



At first glance, *A*, *AR*, and *tOre* all cancel, *DUI* is 1, and the equation reduces to simply the value of *MP*. This is slightly misleading however, because each of these phenomena can be accounted for by sources of information within the ERW supply chain.

**Determining** *A*: The area of mineral application may be determined by a prescription for the area to be applied; or from an as-applied map provided by the applicator; or may come from satellite imagery if taken on a cloud free day immediately after application.

**Determining** *AR*: The application rate should be determined by a rate prescription, supported by an as-applied map, and may be corroborated by pre- and post- application soil measurements.

**Determining** *tOre*: The total amount of mineral applied to the field should be assessed by shipping records. These records should be ultimately traceable to the mill or quarry to achieve mass balance closure for the total amount of mineral applied in the project. An as-applied map may complement this record of mineral applied. Moisture content shall be accounted for, as water is typically a binder to reduce dust in handling and spreading.

**Determining** *MP*: A large body of literature traceable to the DOE and National Labs [2, 7–9] provides a simple expression for the mineral potential (MP) for  $CO_2$  removal based on feedstock elemental composition in terms of MgO% and CaO%, shown in Equation 31.

$$MP \equiv \frac{tCO_2 e}{tOre} = \frac{MW_{CO_2}}{100\%} \cdot \left(\frac{MgO\%}{MW_{MgO}} + \frac{CaO\%}{MW_{CaO}}\right) * V$$
(11)

where:

MgO%	= Mass fraction of magnesium oxide in the mineral.
$MW_{MgO}$	= Molecular weight of magnesium oxide (40g/mol).
CaO%	= Mass fraction of calcium oxide in the mineral.
$MW_{CaO}$	= Molecular weight of calcium oxide $(56g/mol)$ .

$MW_{CO_2}$	= Molecular weight of $CO_2$ (44g/mol).	
V	= Valence of the cations (2 for Mg and Ca)	

Analytical labs typically provide calibrations and validations against traceable standards as a standard set of quality assurance documentation for elemental analysis used to determine *MP*.

**Determining** *DUI*: This value shall be estimated as approximately 1 *if* the soil can be shown to be at a pH where  $\frac{dDIC}{dAlk}$  is within an appropriate range (that is, between 6.2 and 7.5, Figure 3). Aglime additions are often used to bring acidic soils into this pH range. The amount of aglime to add to reach a pH target is known as the lime requirement (*LR*). The LR of soils is commonly determined by used of a soil test; an example of such a calculation is provided in Appendix C.

Thus, determining DUI may be achieved by a combination of (a) a baseline soil test that quantifies soil and buffer pH, (b) a prescription by an agronomist for the lime requirement (LR) of the soil, and (c) an application rate (AR) for the silicate mineral that meets this LR, making use of the CCE of the product applied, which can be determined from (d) an elemental analysis.

#### 8.3.2 Actual CDR

Potential CDR from ERW can be known at the time of application, but actual CDR takes place over time as the acidity in the soil weathers the mineral, bringing cations into solution and taking up DIC in the soil (Figure 1).

Actual CDR shall be computed as:

$$CDR_{actual,t} = CDR_{potential} \cdot f_{sequestered,t}$$
(12)

where:

CDR <sub>actual,t</sub>	= Actual $CO_2$ removal at time <i>t</i> (t $CO_2$ /t $Ore$ ).
CDR <sub>potential</sub>	= Maximum potential $CO_2$ removal (t $CO_2$ /t $Ore$ ).
$f_{captured,t}$	= Fraction sequestered of potential CDR at time $t$ (-).

In this context,  $f_{captured,t}$  quantifies the cations and associated DIC that has been leached below a plane in the soil at time *t* as a fraction of the total cations represented in  $CDR_{potential}$ :

$$f_{captured,t} = \frac{DivAlk_{captured,t}}{DivAlk_{added}}$$
(13)

DivAlk<sub>added</sub> corresponds to the equivalents of charge in divalent cations (Mg and Ca) (i.e. divalent alkalinity) per unit mass of soil  $\frac{eq}{g_{soil}}$ , following the equation:

$$DivAlk_{added} = \left(\frac{MgO\%}{MW_{MgO}} + \frac{CaO\%}{MW_{CaO}}\right)_{added} \cdot V \cdot AR \cdot \frac{1}{d \cdot \rho}$$
(14)

where *d* (units m) represents the depth of the plane defining sequestration  $\rho$  (units g/cm<sup>3</sup>) represents soil bulk density. The units of this expression for DivAlk<sub>added</sub> is therefore as follows:

 $\frac{equivalents}{mass \ soil} = \frac{mass \ oxide}{mass \ ore} \cdot \frac{mol \ oxide}{mass \ oxide} \cdot \frac{equivalents}{mol \ oxide} \cdot \frac{mass \ ore}{area \ soil} \cdot \frac{1}{depth \ soil} \cdot \frac{volume \ soil}{mass \ soil}$ (15)

where *oxide* refers to MgO or CaO as in Equations 31, 33, 20.

#### **Determining** *DivAlk*<sub>added</sub>:

The central challenge in this methodology is the estimation of  $DivAlk_{added}$ , which ultimately determines  $f_{sequestered,t}$ , and thus the amount of carbon removal achieved to date at discrete moments in time (*t*). Equation 14 suggests that  $DivAlk_{added}$  can be determined by knowledge of an elemental analysis and field application rate, or by measurement of soil after application of the mineral amendment.

**Option 1:** *DivAlk*<sub>added</sub> is estimated by the elemental composition of the mineral amendment and measurements of *DivAlk*<sub>post,t</sub>, which is defined as the equivalents of the charge in divalent cations (Mg and Ca) as measured in the soil after mineral application. The same analyses used to determine *MP* may be used to determine the abundance of other elements in the mineral - including elemental composition includes not only Mg and Ca and also analysis of some predetermined project-specific tracers, which could be isotopic tracers or immobile trace elements that provide a record of application rates of mineral soil amendment.

The means of estimating the application rate using an immobile trace element follows, where *Z* represents the concentration of am immobile trace element:

#### **Mineral Amendment Budget:**

$$Z_{post} \cdot Mass_{soil} = Z_{pre} \cdot Mass_{soil} + Z_{rock} \cdot AR_{rock}(kg)$$
(16)

where

$$Mass_{soil} = Area_{soil} \cdot Depth_{soil} \cdot \rho(kg) \tag{17}$$

and

$$AR_{rock} = \frac{Mass_{rock}}{Area_{soil}} (kg/m2)$$
<sup>(18)</sup>

which rearranges to:

$$AR_{rock} = \frac{\left(Z_{post} - Z_{pre}\right) \cdot Mass_{soil}}{Z_{rock}}$$
(19)

From this mineral amendment budget, Equation 20 can be be computed by substituting  $DivAlk_{rock} \cdot AR_{rock}$  for  $DivAlk_{added}$ :

In this expression, *Z* in soil and rock can be calculated from an elemental analysis, e.g. from ICP-MS, and  $Mass_{soil}$  can be determined from Equation 17, where Depth is the depth to which soils are collected for *Z* (e.g. 30cm) and  $\rho$  is bulk density. Bulk density may be determined using empirical or model-based methods, e.g. Saxton and Rawls 2006.  $DivAlk_{added}$  is either measured episodically with soil sampling or continuously with a sensor.

However, because the values for  $DivAlk_{post,t}$  are determined from soil tests ultimately from a small amount of soil, the spatial variation in application rate of the mineral is certain to result in samples where the actual amount of mineral applied deviates deviate from the nominal value. This variation in the actual application rate in the specific sample of soil can in principle dominate the estimate of  $DivAlk_{added}$ .

**Option 2:** *DivAlk*<sub>added</sub> is estimated using the nominal application rate and the concentration of Mg and Ca in the rock material. Nominal application rate may be determined using records from an applicator, or from knowledge of the amount of mineral delivered to the field and the area of the field. Concentration of Mg and Ca can be determined using an elemental analysis, e.g. from ICP-MS.

#### **Determining** *DivAlk*<sub>captured</sub>

Determining the amount of alkalinity captured and therefore the fraction of weathering that has occurred can be determined in several ways, some of which are developed as of the time of this writing and some of which are yet to be discovered or developed.

**Option 1:** *DivAlk*<sub>*captured*,*t*</sub> is calculated as (Figure 4):

 $DivAlk_{captured,t} = DivAlk_{pre} + DivAlk_{added} - DivAlk_{losses} - DivAlk_{post,t}$ (20)

where:

DivAlk <sub>captured,t</sub>	= Divalent alkalinity captured (i.e. sequestered) ( $eq/g$ ).
DivAlk <sub>pre</sub>	= Divalent alkalinity in the pre-application baseline soil ( $eq/g$ ).
DivAlk <sub>added</sub>	= Divalent alkalinity added in the silicate mineral amendment ( $eq/g$ ).
DivAlk <sub>losses</sub>	= Divalent alkalinity losses from plant uptake and charge-balance with non-DIC cations (e.g. $NO_3^-$ , $SO_3^-$ or $Cl^-$ ) (eq/g).
DivAlk <sub>post,t</sub>	= Divalent alkalinity in the post-application soil at time $t$ (eq/g).

Figure 4: Simplified budget equation of divalent cations that remove CO<sub>2</sub>.



**Determining**  $DivAlk_{pre}$  **and**  $DivAlk_{post,t}$ : The elemental abundance of Mg and Ca in soils shall be determined from a soil test through analysis via total fusion- inductively coupled plasma mass spectrometry. The difference between  $DivAlk_{pre}$  and  $DivAlk_{post,t}$  quantifies the leached base cations that have in fact left the topsoil control volume. More specifically,  $DivAlk_{post,t}$  allows for a direct measurement of persistent base cations; this accounts for various subsurface soil processes, including but not limited to adsorption to minerals, secondary mineral formation, and carbonate-based precipitation inefficiencies.

$$DivAlk_{pre/post} = \left(\frac{Mg\%}{MW_{Mg}} + \frac{Ca\%}{MW_{Ca}}\right)_{soil} \cdot V$$
<sup>(21)</sup>

where:

DivAlk <sub>pre/post</sub>	= Divalent alkalinity in the pre- or post-application baseline soil $(eq/g)$ .
Mg%orCa%	= Mg or Ca content of the soil (g Mg / g soil or g Ca / g Soil).
MW <sub>Mg</sub> orMW <sub>Ca</sub>	= Molecular weights of Mg or Ca $(g/mol)$ .
V	= Valence of Mg or Ca (eq/mol).

This expression has units  $\frac{eq}{g_{soil}}$ :

 $\frac{equivalents}{mass \ soil} = \frac{mass \ cation}{mass \ soil} \cdot \frac{mol \ cation}{mass \ oxide} \cdot \frac{equivalents}{mol \ cation}$ (22)

**Option 2:**  $DivAlk_{captured}$  is estimated using a lysimeter or other device that is used to capture the soil water.  $DivAlk_{captured}$  is either measured episodically with sampling or continuously with a sensor.

#### **Lossy Cation Budget:**

$$DivAlk_{sequestered,t} = DivAlk_{pre} + DivAlk_{rock} \cdot AR_{rock} - DivAlk_{losses} - DivAlk_{post,t}$$
(23)

#### **Determining** *DivAlk*<sub>losses</sub>:

*DivAlk*<sub>losses</sub> is calculated as:

$$DivAlk_{losses} = DivAlk_{uptake} + DivAlk_{other}$$
<sup>(24)</sup>

where

DivAlk <sub>uptake</sub>	= Divalent alkalinity losses from plant uptake $(eq/g)$ .
DivAlk <sub>other</sub>	= Divalent alkalinity charge-balance with non-DIC anions (e.g. $NO_3^-$ , $SO_3^-$ or $Cl^-$ ) (eq/g).

**Determining** *DivAlk*<sub>uvtake</sub>:

 $DivAlk_{uptake}$  assumes that plant uptake of Mg and Ca does not distinguish between rock vs. soil nutrients; therefore, the plant uptake fraction of divalent uptake is calculated as the total plant uptake times the fraction of Mg from the rock.

(25)

 $DivAlk_{uptake} = DivAlk_{uptake,Mg} + DivAlk_{uptake,Ca}$ 

where

DivAlk <sub>uptake,Mg</sub>	<pre>= rockMg / (rockMg + soilMg ) * plantuptakeMg</pre>
DivAlk <sub>uptake,Ca</sub>	= rockCa / (rockCa + soilCa ) * plantuptakeCa

rock(Mg,Ca)	= the Mg or Ca content of the rock $(g/m^2)$
soil(Mg,Ca)	= the Mg or Ca content of the soil $(g/m^2)$

plantup take(Mg, Ca) = mass of Mg or Ca content taken up by the plant (g/m2).

#### Determining plantuptake(Mg, Ca)

When CDR is being calculated for a field with annual plant starting before planting,

$$plantuptake(Mg, Ca) = plant(Mg, Ca)$$
(26)

where

plant(Mg,Ca) = the mass of Mg or Ca in the plant

When CDR is being calculated in other conditions, such as when rock has been applied after a plant has already been established, or when CDR is being calculated from a later time point than application

$$plantup take(Mg, Ca) = plant(Mg, Ca)_{t2} - plant(Mg, Ca)_{t1}$$
(27)

#### **Determining plant(Mg, Ca)**:

plant(Mg,Ca) may be determined using one of the following options:

**Option 1:** Plant samples of leaves shall be collected at peak biomass and root samples should be collected at peak biomass or pre-harvest, and analyzed for C, N, Mg and Ca content. Total mass of shoots should be quantified, and the root:shoot ratio can be estimated by root N : grain N, root N : shoot N, and/or C:N ratio following Ordonez et al. 2020, European Journal of Agronomy. From the root:shoot ratio, total mass of shoots, and the Mg and Ca content of the roots and the shoots, the total plant Mg and Ca can be calculated.

**Option 2:** Quantify the total mass of the shoots and leaf Mg and Ca content. Assume literature values of root nutrient content and root:shoot rations, and calculate the Mg and Ca content of the total plant as above.

**Option 3:** Use maximum literature values of the fraction of soil Mg and Ca that is taken up by the plant over a growing seasons.

#### **Determining** *DivAlk*<sub>other</sub>:

The divalent cations in the soil solution do not preferentially bind with bicarbonate, and can in fact leach out of the system with other anions that may weather the silicate rock, such as through nitrate ion-pair leaching.

$$DivAlk_{other} = DivAlk_{sequestered,t} * f_{other}$$

where

fother

= Fraction of divalent alkalinity charge-balanced with non-DIC cations

(28)

#### **Determining** *f*<sub>other</sub>:

**Option 1:** Using a lysimeter installed in the top 30 cm soil control volume, capture the volume of soil water leachate from a small portion of the field. This collection should be performed on

both applied- and control- fields. The resultant difference in measured inorganic nitrate (concentration of ammonia + concentration of nitrate) between applied- and control- fields allows for the quantification of additional nitrate leaching induced by the enhanced rock weathering process. The resultant difference value of inorganic nitrate concentration is converted from ppm (mg/L) to a molar quantity (mol/L) through division of N molar mass (14 g/mol) and a factor of 1000. The final molar quantity of inorganic nitrate difference is multiplied by 2 as a conservative estimate; this follows the assumption that all nitrogen is ultimately transformed into the form of  $NO_3^-$ , which requires 2 molecules to charge-balance a  $Mg^{2+}$  or  $Ca^{2+}$  cation.

**Option 2:** Conservatively estimate the fraction of the divalent cations that are bonded to other anions than DIC in the water. Here we assume a value of 10% based on literature review (citation needed).

#### 8.4 System Loss

In the context of enhanced mineral weathering on land, there is a system loss of CO<sub>2</sub> when the *DUI* in Equation 10 (depicted in Figure 3) drops below its nominal value of ~ 1, owing to shifts in the carbonate system equilibrium. This system loss is the reversal of CO<sub>2</sub> captured. It is widely known that the value of DUI in the ocean is below ~ 0.9, meaning that 10% of  $CDR_{potential}$  will ultimately be returned back to the atmosphere as a natural and predictable phenomenon. This loss fraction (*LF*) is appreciated as simply the difference between the the initial and final  $\frac{dDIC}{dAlk}$ , which are referred to as initial DUI and the DUI rentention index (DRI):

$$LF = DUI - DRI \tag{29}$$

where:

LF	= Leakage Fraction (%).
DUI	= DIC uptake index in soils where weathering takes place, equivalent to $\frac{dDIC}{dAlk}$ , the moles of DIC taken up by soil solution per marginal unit of added alkalinity.
DRI	= DIC retention index in fresh and marine waters, also equivalent to equivalent to $\frac{dDIC}{dAlk}$ , where dissolved cations and inorganic carbonates added from EW are present.

Total system loss (SL, in tCO<sub>2</sub>e) can be computed as:

$$SL = CDR_{actual} \cdot (1 - LR) \tag{30}$$

The timing of the actual leakage is subject to large variation; it could be in months, if a field empties directly into surface waters, or 30 or more years if the depth to groundwater is large enough.

Given that DUI is defined to be equivalent to 1, by applying mineral at a rate sufficient to bring the soil pH into the range 6.5 - 7.2, the challenge in leakage estimation is to determine (a) the ultimate value of DRI in the final storage repository and (b) determine if any transient conditions exist in transport to the final storage repository that would result in DRI being lower than DRI in the final storage locale.

Two trivial cases where DRI is much lower than the oceanic value are readily identified: arid inland basins that don't drain to the ocean, where dissolved carbonates are precipitated as they evaporate (final DRI value  $\sim 0.5$ ) and high latitude inland basins where lake waters are extremely acidic (final DRI value  $\sim 0.0$ ). Such application locales are not recommended for EW because of the significant opportunity for leakage.

The remaining cases require consideration of the carbonate system within the fresh and marine waters as DIC and alkalinity are transported ultimately to the ocean.

#### 8.4.1 River DRI

River DRI may be calculated in the following ways:

**Option 1:** A sensor network is set up to monitor the downstream river chemistry for pH, Alkalinity and  $pCO^2$ . Records should be monitored monthly until more information has been collected, at which point less frequent monitoring may take place.

Figure 5: US River water samples: DRI vs. pH.

**Option 2:** For calculating river DRI in the United States, data may be used from the Global River Chemistry Database (GLORICH) [10] for rivers in the US between 1980-2007. This dataset includes all the sampling stations for rivers in US, and hence all those within the Mississippi basin. The core parameters used are Alkalinity and  $pCO^2$ . Auxiliary parameters: water temperature, salinity of fresh water, and pressure. Sources of data for each parameter are given in Table 2.

Variable	Source
TA	USGS
$pCO^2$	NOAA [11]
Temperature	USGS
Salinity	N/A
Pressure <sup>01</sup>	USGS

Table 2: River DRI Input Sources

River DRI for all river water samples logged within the GLORICH database show that greater than 99.9% of samples have DRI > 0.85, as seen in Figure 5.

#### 8.4.2 Oceanic DRI

For oceanic DRI calculate two versions:

- A global oceanic baseline DRI
- A localized oceanic annual DRI, at 1 x 1 degree spatial resolution.

#### 8.4.3 Global oceanic baseline DRI

The global oceanic baseline is calculated using the following summary values and comes out to 0.85.

Ocean Parameters	Value Used	Range	Source
Ocean pH	8.08	7.9-8.25	[12]
Ocean Salinity	35	34-35	[13]
Ocean Temperature $(C)$	16.1	16-19	[14]
$pCO^2$	400	390-410	[11]

Table 3: Global Ocean DRI Parameter Values

#### 8.4.4 Localised annual oceanic DRI

For the localized annual DRI, the two system variables used to calculate the carbonate states are TA and pH. Auxiliary variables are seawater temperature and salinity and we take pressure = 0 at the ocean surface. We use data from the OceanSODA-ETHZ [15] dataset, which provides chosen variables at high spatial resolution, and for the years 1985-2018. Data is first processed by taking the weighted temporal average for each variable of interest to create an annual mean before DRI is calculated again using PyCO2SYS.

Visualization of the mean of the annual means can be seen in Figure 6.

<sup>&</sup>lt;sup>01</sup>Calculated from altitude of sample



Figure 6: Localised mean oceanic DRI for years 1958 - 2018, at 1 x 1 degree resolution

Land Parameters	Value
Land pH	6.5 - 7.2
Land Temperature (°C)	25
Net Valence	2

Table 4: Soil DRI Parameters

#### 8.4.5 Soil DRI

For agricultural soils with a pH between 6.5-7.2, DRI is calculated using the parameters land pH, land temperature, and net valence, and comes out at ~0.999. Parameters are given in Table 4 for silicate rocks.

# 9 Monitoring

9.1	Data and	<b>Parameters</b>	Available	at	Validation
-----	----------	-------------------	-----------	----	------------

Parameter	Unit	Source	Value applied	Explanation/Comments
Project				
Emissions			TA7:11	Enclosience featen af
<i>EF<sub>grid,Q</sub></i>	tCO2/MWH	eGrid for	will vary, depending	emissions factor of grid to dotormino CO2
		or UN-	For example see:	impact of electricity use
L1 grid,M		FCCC data	https://www.epa.gov/	required by the project
		(CDM)	egrid/summary-data	(quarrying, milling,
		(02111)		etc.).
$EF_{fuel,i,Q}$	tCO2eq/unit	IPCC or	Will vary depend-	Emissions factor of each
and		EPA de-	ing on fuel. See:	type of fossil fuel re-
$EF_{fuel,i,M}$		faults	https://www.epa.gov/	quired to implement
			environment	the project (quarrying,
		IDCC	/emissions/ $co2_vol_mass.pl$	<i>p</i> milling, etc.).
$EF_i$ and	tCO2eq/unit	IPCC or	Will vary depend-	Emissions factor of each
EF <sub>i,j</sub>		EPA de-	ing on fuel. See:	type of fossil fuel (eg:
		launs	onvironment	gasonine of diesel) re-
			/emissions/co2 of ass n	therials across transport
			$\gamma$ emissions $\gamma$ co $2_v o t_m uss. pr$	leg i This parameter
				can also be used for fos-
				sil fuel required for field
				application.
EF <sub>ton-mile.m</sub>	tCO2/ton-	DEFRA	See Table A.1 of Appen-	Emissions factor to
	miles	data (EPA	dix B	transport a ton of
		data may		minerals one mile by
		also be		transport mode m. This
		used)		option can be used as
				an alternative to calcu-
				late transport emissions
				based on the distance
				traveled by each ton of
ETD	Litoro par	Contrac??	5 97 I /LI	ore.
	bour	Source:	0.07 L/ П	fuel usage per unit time
	noui			on a 50HP motor. Other
				motor sizes will be dif-
				ferent.
ТРМРА	hours/-	Source??	Based on two tons per	Application time per
	tOre/acre		acre in 5 minutes, this	mass of mineral applied
			figure would be 5 tons	per area, based on a
			per hectare in 12.5 min-	50HP motor. Other mo-
			utes	tor sizes will be differ-
				ent.

Table 5: Data and Parameters available at validation: Project emissions

Parameter	Unit	Source	Value applied	Explanation/Comments
Carbon				
Dioxide				
Removals				
$MW_{MgO}$	g/mol	N/A	40	Used to determine MP,
				mineral potential of the
				applied silicate, which
				is a key part of assess-
				ing the overall CDR po-
3.6347	/ 1			tential.
MW <sub>CaO</sub>	g/mol	N/A	56	Used to determine MP,
				mineral potential of the
2 4147	/ 1		4.4	applied silicate.
MW <sub>CO2</sub>	g/mol	N/A	44	Used to determine MP,
				mineral potential of the
NZ			2 for Ma and Co	Valance of estions used
V	number	IN/A	2 for Mg and Ca	to dotormino MP
I Dand H	mU	Coilteat		nH and nH buffer and
L, D апа п	рп	Son test	vviii vary	pH goal, pH builer and
				determine lime require
				ment (IR) This can be
				determined by soil test-
				ing
CCE	number	Mineral	Will Vary	Calcium Carbonate
		elemental		Equivalent of silicates
		analysis		in references to com-
		]		mon aglimes. See Table
				1.

Table 6: Data and Parameters available at validation: Carbon Dioxide Removals

### 9.2 Data and Parameters Monitored

Parameter	Unit	Source	Explanation/Comments ment Techniques	and	Measure-
Project Emissions					

$TPY_O$ and	Tons of Ore	Project owner/s-	Annual production of all minerals
tOre,j		cale readings	processed and used by the project as
			determined by scales (at the quarry)
			that are calibrated in accordance with
			manufacturer recommendations. This
			information is be separated by different
			transport legs j so the end destination
			of all tons of ore are compiled into a
			spreadsheet that can be reviewed by
			a verifier. This will also provide the
			tons of ore used per project unit (farm),
			which can determine if any ore has been
			lost between the quarry, mill and farm.
			Knowing the quantity of minerals per
			farm is also required for AR (application
			rate in tons of ore per hectare). Project
			developer will create a data management
			system to track every ton of mineral from
			the quarry to the milling facility to the
17 1		<b>T</b> 1 4 1 4 1 411	farm.
$V_{grid,Q}$ and	MWH	Electricity bills or	Quantity of electricity used at the quarry,
V <sub>grid</sub> ,M		conservative esti-	milling and other purposes required to
		tared congrately	implement the project.
Verand	Dependent	Fuel receipts or	Quantity of fuel used at the guarry
V <sub>fuel</sub> ,Q and	on fuel type	utility gas hills or	milling and other purposes required to
• fuel,M	(gallons	conservative esti-	implement the project
	MMBTU.	mates if not calcu-	implement die project.
	etc.)	lated separately	
$D_i$	Miles	Project owner	Distance of transport leg j as calculated
)		)	by GPS tracking of vehicle or using ap-
			propriate app, such as Google Maps. All
			end destinations of the ore and (if differ-
			ent transport modes are used) the distance
			from one leg to another – quarry to mill
			to farm – should be entered into a data
			management system and archived for ver-
			ification purposes.
$V_{i,j}$	Gallons	Project owner	Quantity of gasoline or diesel (or kWhs if
			electric vehicles) needed to transport ma-
			terials across transport leg j.

# Table 7: Data and Parameters Monitored: Project emissions

Parameter	Unit	Source	Explanation/Comments	and	Measure-
			ment Techniques		

Carbon			
Dioxide			
Removals			
A	Hectares	Project owner	Area of mineral application during the project. Additional lands can be added throughout the project, but the project owner should keep .kml files, satellite im- age or similar visuals, along with GPS co- ordinates or physical address, to denote the area of land coverage per farm and across the entire project boundary. These files should be made available to a verifier.
AR and	Tons of ore	Farmer and	Application rate of mineral as measured
thus tOre	per hectare	project owner	by farmer records, applicator measure-
	and total		ments or similar approach and validated
	metric tons		by project owner in a similar manner
	of mineral		to how farmers determine fertilizer ap-
	applied		plication rates per ha. Another option
	over area A		would be to measure ITEs, through base-
			line soil testing. This information should
			be crossed-checked with sales and ship-
			ping.

Soil testing	Various	Project own-	In addition to pH, soil testing will mea-
	units in-	er/laboratory	sure Mg and Ca content of the soil (to de-
	cluding pH,	results	termine rockMg and soilMg) as well as
	Mg and		depth of area where sequestration takes
	Ca content,		place (d) and the bulk density of the soil
	soil depth		in g/cm3.
	and density.		Soil testing should be done prior to the
	Used to		project start date (baseline testing) as well
	determine		as annually. Project proponents should de-
	divalent		velop a testing protocol in terms of how
	alkalinity		many tests should be required per farm
	nre and		based on the level of homogeneity of each
	post project		field and across different fields within
	postpioject		the project houndary. Cuidance around
			such protocols can be developed follow-
			ing guidance in VM0042 as well as the
			ang guidance in vivio042, as well as the
			Sources below.
			Soli sampling should follow established
			best practices, such as: 1) Cline, M.G. 1944.
			Principles of soil sampling. Soil Science.
			58: 2/5 – 288. 2) Petersen, K.G., and Calvin,
			L.D. Sampling. In A. Klute, editor, 1986.
			Methods of Soil Analysis: Part I—Phys-
			ical and Mineralogical Methods. SSSA
			Book Ser. 5.1. SSSA, ASA, Madison, WI.
			3) Bulk density may be determined using
			empirical or model-based methods, e.g.
			Saxton and Rawls 2006.
			Lab results should be made available to
			the verifier upon request and all test re-
			sults should be archived.
Testing of	N/A	Project own-	Used for measurements of $Div_{Alkpost,t}$ and
tracers		er/laboratory	the elemental composition of the mineral
		results	amendment. This same elemental analy-
			sis can be used to determine MP as well
			(mineral potential of the applied silicate
			(tCO2/tOre) in the case of elemental trac-
			ers; isotopic analysis are required for iso-
			topic tracers.
	g/m2	Project Owner	Mass of Mg or Ca in the plant to deter-
plant(Mg,Ca	)		mine plant uptake. Samples of leaves and
			roots should be taken as articulated in Op-
			tion 1 and 2 of plantuptake(Mg,Ca). Max-
			imum literature values of the fraction of
			soil Mg and Ca may also be used (Option
			3) – sources shall be provided to the VVB.

fother	Fraction	Project Owner	Using a lysimeter, capture the volume of
			soil water from a small portion of the field
			to quantify the ratio of cations:DIC in the
			soil water. This ratio should be close to
			but not exceeding 2. Option 2 is to use a
			default of 10%.

Table 8: Data and Parameters Monitored: Carbon Dioxide Removals

## References

### References

- [1] Bide TP, Styles MT, Naden J (2014) An assessment of global resources of rocks as suitable raw materials for carbon capture and storage by mineralisation. *Applied Earth Science* 123(3):179–195. Publisher: Taylor & Francis.
- [2] Beerling DJ, et al. (2020) Potential for large-scale CO 2 removal via enhanced rock weathering with croplands. *Nature* 583(7815):242–248. Publisher: Nature Publishing Group.
- [3] Blanc-Betes E, et al. (2021) In silico assessment of the potential of basalt amendments to reduce N2O emissions from bioenergy crops. *GCB Bioenergy* 13(1):224–241. Publisher: Wiley Online Library.
- [4] Stebbins SA, Leinart JB (2011) Cost estimating for surface mines. *SME Mining Engineering Handbook* :281–293.
- [5] US DOE Office of Energy Efficiency and Renewable Energy (2013) Limestone and Crushed Rock. *Energy and Environmental Profile of the U.S. Mining Industry* (Department of Energy), , , .
- [6] Strefler J, Amann T, Bauer N, Kriegler E, Hartmann J (2018) Potential and costs of carbon dioxide removal by enhanced weathering of rocks. *Environmental Research Letters* 13(3):034010. Publisher: IOP Publishing.
- [7] Renforth P (2012) The potential of enhanced weathering in the UK. *International Journal of Greenhouse Gas Control* 10:229–243. Publisher: Elsevier.
- [8] O'Connor K, Dahlin DC, Rush GE, Gerdemann SJ, Penner LR (2004) Energy and Economic Considerations for Ex Situ Aqueous Mineral Carbonation. Proc. 29 th International Technical Conference on Coal Utilization and Fuel Systems. *Coal Technology Association, Clearwater, FL*.
- [9] Goff F, et al. (1997) Preliminary investigations on the carbon dioxide sequestering potential of the ultramafic rock. Los Alamos National Lab., NM (United States), Technical report.
- [10] Hartmann J, Lauerwald R, Moosdorf N (2014) A brief overview of the GLObal RIver CHemistry Database, GLORICH. *Procedia Earth and Planetary Science* 10:23–27. Publisher: Elsevier.
- [11] Dlugokencky E, Tans P Globally averaged marine surface annual mean data, . https://doi.org/ gml.noaa.gov/ccgg/trends/
- [12] Raven J, et al. Ocean acidification due to increasing atmospheric carbon dioxide 2005, .
- [13] Boyer TP, et al. World ocean atlas 2018, Accessed Jan 2022 URL https://www.ncei.noaa. gov/archive/accession/NCEI-WOA18.
- [14] Zhang HM, B Huang JL, Menne M, Smith TM Noaa global surface temperature dataset version 5, . https://doi.org/10.25921/9qth-2p70. Accessed Jan 2022
- [15] Gregor L, Gruber N (2021) OceanSODA-ETHZ: A global gridded data set of the surface ocean carbonate system for seasonal to decadal studies of ocean acidification. *Earth System Science Data* 13(2):777–808. https://doi.org/10.5194/essd-13-777-2021

# Appendices A Electricity Grid Emissions Factors

Table A1: US Emissions Factors in kgCO<sub>2</sub>e/kWh

Area	Region	Value
US: Average		0.453
US: Alabama (AL)	SERC - South	0.414
US: Alaska (AK)	ASCC - Alaska Grid	0.436
US: Arizona (AZ)	WECC - Southwest	0.463
US: Arkansas (AR)	SERC - South	0.581
US: California (CA)	WECC- California	0.201
US: Colorado (CO)	WECC - Rockies	0.653
US: Connecticut (CT)	NPCC - New England	0.243
US: Delaware (DE)	RFC - East	0.429
US: Florida (FL)	FRCC - All	0.452
US: Georgia (GA)	SERC - South	0.444
US: Hawaii (HI)	HICC - Oahu	0.729
US: Idaho (ID)	WECC - Rockies	0.077
US: Illinois (IL)	MRO- East	0.390
US: Indiana (IN)	RFC - West	0.834
US: Iowa (IA)	MRO - East	0.514
US: Kansas (KS)	SPP- North	0.475
US: Kentucky (KY)	SERC - Tennessee Vallev	0.875
US: Louisiana (LA)	SERC - South	0.400
US: Maine (ME)	NPCC - New England	0.128
US: Maryland (MD)	RFC - East	0.401
US: Massachusetts (MA)	NPCC - New England	0.350
US: Michigan (MI)	RFC - Michigan	0.532
US: Minnesota (MN)	MRO - East	0.478
US: Mississippi (MS)	SERC - South	0.438
US: Missouri (MO)	SERC - South	0.817
US: Montana (MT)	WECC - Rockies	0.556
US: Nebraska (NE)	MRO-West	0.676
US: Nevada (NV)	WECC - Rockies	0.356
US: New Hampshire (NH)	NPCC - New England	0.146
US: New Jersey (NI)	RFC - East	0.239
US: New Mexico (NM)	WECC - Southwest	0.639
US: New York (NY)	NPCC - LINYC/Upstate NY	0.200
US: North Carolina (NC)	SERC - Virginia/Carolinas	0.383
US: North Dakota (ND)	MRO-West	0.723
US: Ohio (OH)	RFC - West	0.634
US: Oklahoma (OK)	SPP- South	0.426
US: Oregon (OR)	WECC - Northwest	0.150
US: Pennsylvania (PA)	RFC - West	0.376
US: Rhode Island (RI)	NPCC - New England	0.414
US: South Carolina (SC)	SERC - Virginia/Carolinas	0.303
US: South Dakota (SD)	MRO-West	0.248
US: Tennessee (TN)	SERC - Tennessee Valley	0.357
US: Texas (TX)	ERCOT - All	0.469
US: Utah (UT)	WECC - Rockies	0.767
US: Vermont (VT)	NPCC - New England	0.027
US: Virginia (VA)	SERC - Virginia/Carolinas	0.354
US: Washington (WA)	WECC - Northwest	0.095
US: Washington DC (DC)	RFC - East	0.210
US: West Virginia (WV)	SERC - Virginia / Carolinas	0.935
US: Wisconsin (WI)	MRO - East	0.666
US: Wyoming (WY)	WECC - Rockies	0.983

Source: United States EPA eGrid Database (Published: Jan 2020. Revised: Mar 2020) URL: https://www.epa.gov/energy/emissions-generation-resource-integrated-database-egrid

# **B** Transportation Emissions Factors

Transport Type	Size	kgCO <sub>2</sub> e	kgCO <sub>2</sub>	kgCH <sub>4</sub>	kgN <sub>2</sub> O
Cargo Ship/Bulk	200,000+ dwt	0.00254	0.00250	0.00000	0.00003
0	100,000–199,999 dwt	0.00304	0.00300	0.00000	0.00004
	60,000–99,999 dwt	0.00416	0.00410	0.00000	0.00006
	35,000–59,999 dwt	0.00578	0.00570	0.00000	0.00008
	10,000–34,999 dwt	0.00801	0.00790	0.00000	0.00011
	0–9999 dwt	0.02961	0.02920	0.00001	0.00040
	Average	0.00354	0.00349	0.00000	0.00005
Cargo Ship/Handy	10,000+ dwt	0.01207	0.01190	0.00000	0.00016
	5000–9999 dwt	0.01602	0.01580	0.00001	0.00022
	0–4999 dwt	0.01409	0.01390	0.00000	0.00019
	10,000+ dwt 100+ TEU	0.01115	0.01100	0.00000	0.00015
	5000–9999 dwt 100+ TEU	0.01774	0.01750	0.00001	0.00024
	0–4999 dwt 100+ TEU	0.02008	0.01980	0.00001	0.00027
	Average	0.01323	0.01305	0.00000	0.00018
Cargo Ship/Container	8000+ TEU	0.01267	0.01250	0.00000	0.00017
	5000–7999 TEU	0.01683	0.01660	0.00001	0.00023
	3000–4999 TEU	0.01683	0.01660	0.00001	0.00023
	2000–2999 TEU	0.02028	0.02000	0.00001	0.00027
	1000–1999 TEU	0.03255	0.03210	0.00001	0.00044
	0–999 TEU	0.03681	0.03630	0.00001	0.00050
	Average	0.01614	0.01592	0.00001	0.00022
Heavy Goods Vehicle	Rigid (>3.5 - 7.5 tonnes)	0.52043	0.51410	0.00010	0.00623
	Rigid (>7.5 tonnes-17 tonnes)	0.36835	0.36388	0.00007	0.00440
	Rigid (>17 tonnes)	0.18306	0.18084	0.00004	0.00219
	All rigids	0.21275	0.21017	0.00004	0.00254
	Articulated (>3.5 - 33t)	0.14179	0.13932	0.00002	0.00245
	Articulated (>33t)	0.07773	0.07638	0.00001	0.00134
	All artics	0.07936	0.07798	0.00001	0.00137
	All HGVs	0.10650	0.10487	0.00002	0.00161
Rail	Freight train	0.02556	0.02531	0.00002	0.00023

Table A2: Transport Emissions Factors in kgCO<sub>2</sub>e/tonne-km

Source: DEFRA (Published: June 2021) URL: https://www.gov.uk/government/publications/greenhouse-gas-reporting-conversion-factors-2021

### C Determination of crop lime requirement

The need for conditioning the pH of soils is widespread, and consequently there are many resources for guiding applications of limestone to raise pH and gypsum to lower pH. Examples can be found through cooperative extension in nearly every state. Illinois (link) and Delaware (link) have particularly good resources.

Our focus is in determining lime requirements in acidic soils. Lime requirements make use of soil tests that combine the soil pH, the buffer pH, and the target pH for the crop under consideration. One such method, known as SMP For the widely used Shoemaker-McLean-Pratt (SMP) soil analysis method for example, *LR* is calculated as:

$$LR = 1250 + (((L - 0.3) - H) * 1820) + ((6.95 - B) * 5260)$$
(31)

where:

L	= pH goal (dependent on the crop)
Н	= actual pH of the soil (1:1 in water).
В	= buffer pH (method dependent; a measure of exchangeable cations)

Note that the *LR* is based on application of a material with a Calcium Carbonate Equivalence (CCE) of 1, based on the neutralizing potential of pure calcite (units eq/g). The neutralizing potential of any particular silicate mineral may be considerably less, depending on its cation concentration.

In general, the neutralizing equivalent of calcite is calculated as:

$$NE_c = \frac{CaO_c}{MW_{CaO}} \cdot V \tag{32}$$

where:

$NE_c$	= Neutralizing equivalent of $CaCO_3$ (eq/g)
CaO <sub>c</sub>	= Mass fraction of calcium oxide in CaCO <sub>3</sub> (56.03%).
MW <sub>CaO</sub>	= Molecular weight of calcium oxide (56g/mol).
V	= Valence of the cations (2 for Mg and Ca).

The neutralizing equivalent of any mineral *m* can then be calculated as:

$$NE_m = \left(\frac{CaO_m}{MW_{CaO}} + \frac{MgO_m}{MW_{MgO}}\right) \cdot V$$
(33)

where  $CaO_m$  and  $MgO_m$  are derived from an elemental analysis of the mineral to be used. The CCE is then calculated by computing the ratio  $\frac{NE_m}{NE_c}$ . The neutralizing value of common carbonates used as aglime is provided below, alongside the neutralizing value for common silicates used for ERW.

		C	Н	0	Si	Са	Mg	CaO	MgO	CCE
Compound	MW	12	1	16	28	40	24	56	40	
	g/mol	# of atoms					mass %			
CaCO <sub>3</sub>	100	1		3		1		56		1
MgCO <sub>3</sub>	84	1		3			1		47	1.19
CaO	56			1		1		1		1.79
Ca(OH) <sub>2</sub>	74		2	2		1		75		1.35
(CaxMg)CO <sub>3</sub>	92	1		3		0.5	0.5	30	22	1.09
CaSiO <sub>3</sub>	116			3	1	1		48		0.86
Mg <sub>2</sub> SiÕ <sub>4</sub>	140			4	1		2		46	1.14
Basalt								10	8	0.38

Table A3: Calcium Carbonate Equivalent of silicates in references to common aglimes.

### **D** Derivation of DRI

 $CO_2$  in the atmosphere is dissolved into the ocean, where it can speciate into other forms including carbonate ( $CO_3^{2-}$ ) and bicarbonate ( $HCO_3^{-}$ ). The dissolution of gaseous, atmospheric  $CO_2$  into dissolved  $CO_2$  is based on a solubilization coefficient that is inversely related to the temperature of the surface ocean and is proportional to the partial pressure of  $CO_2$  in the surface ocean. The equation follows Henry's law, which is that the dissolved gas in solution is proportional to it's partial pressure. Thus,  $K_h$ , the solubility of  $CO_2$  in water is defined as:

$$[\mathrm{CO}_2] = \mathrm{K}_0(\mathrm{T},\mathrm{S}) \cdot \mathrm{p}\mathrm{CO}_2 \tag{34}$$

Computed as:

$$\ln K_h = 9345.17/T - 60.2409 + 23.3585 \ln (T/100)$$

$$+ S[0.023517 - 0.00023656T + 0.00047036(T/100)^2]$$
(35)

where T is temperature in °K, S is salinity in UNITS, and units are mol/kg. The partial pressure,  $pCO_2$  can be closely approximated by the fugacity of  $[CO_2]$ ,  $f[CO_2]$  [?].

Once dissolved,  $CO_2$  speciates into the other forms of DIC (including carbonate  $CO_3^{2-}$  and bicarbonate  $HCO_3^{-}$ ) based on equilibrium kinetics.  $K_1^*$  is the stoichiometric equilibrium constant of the first dissociation of carbonic acid, between carbon dioxide and bicarbonate, defined as:

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]}$$
(36)

and K<sub>2</sub>\* is the stoichiometric equilibrium constant of the first dissociation of carbonic acid, between bicarbonate and carbonate, defined as:

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^{-}]}$$
(37)

These constants can be computed as:

$$\ln K_{1} = 2.83655 - 2307.1266/T - 1.5529413 \ln T$$

$$- (0.207608410 + 4.0484/T)\sqrt{S}$$

$$+ 0.0846834S - 0.00654208S^{3/2} + \ln (1 - 0.001005S)$$
(38)

and

$$\ln K_{2} = -9.226508 - 3351.6106/T - 0.2005743 \ln T$$

$$- (0.106901773 + 23.9722/T)\sqrt{S}$$

$$+ 0.1130822S - 0.00846934S^{3/2} + \ln (1 - 0.001005S)$$
(39)

where T is in °K and units are mol/kg. [?]

Dissolved organic carbon (DIC) is the sum of all dissolved forms, including CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, and is notated as DIC or  $\sum CO_2$ , as defined in the following equation:

$$DIC = [CO_2] + [HCO_3^{-}] + [CO_3^{2-}]$$
(40)

The relative proportion of these three species of DIC is driven by temperature and salinity. The speciation of DIC in turns impacts the concentration of  $[H^+]$  in the water, and therefore impacts the pH. These relationships are shown in Figure 7 below.



Figure 7: DIC speciation vs. pH, showing CO<sub>2</sub>,  $HCO_3^-$ , and  $CO_3^{2-}$ , on a log scale (left) and as a fraction of total DIC (right)

Carbonate alkalinity (CA) is the sum of the total charges on the carbon forms, which is:

$$CA = [HCO_3^{-}] + 2 * [CO_3^{2-}]$$
(41)

 $CO_3^{2-}$  has twice the influence on CA as  $HCO_3^{-}$  because it has two negative charges, while  $HCO_3^{-}$  only has one.

The equivalence point is defined as the point at which carbonate alkalinity is 0, so

$$[H^+] = [HCO_3^{-}] + 2 * [CO_3^{2-}] + [OH^-].$$
(42)

The equivalence point is also known as the proton condition, which can be experimentally determined via titration.

Total alkalinity is similar but includes the influence of other ions, including Boron. Define total alkalinity (TA) as the sum of proton acceptors minus proton donors (for now ignoring minor species), and is interpreted as a charge imbalance:

$$TA = [HCO_3^{-}] + 2 \cdot [CO_3^{2-}] + [OH^{-}] - [H^{+}]$$
(43)

This definition of TA is has units of meq/kg, where meq is the charge weighted molar concentration of the species under consideration:

$$TA = \sum_{j} z_{j}[c_{j}] \tag{44}$$

where *c* j is an ion of interest, c is the concentration of that ion (units mol/kg) *z* is the valence of that ion (1, 2, or 3, positive or negative), hence 2 for  $[CO_3^{2-}]$  and -1 for for  $[H^+]$ .

We interpret alkalinity as the charge imbalance of conservative cations over conservative anions, and therefore that alkalinity is a conserved quantity. The charge imbalance between the cations and the anions in the ocean is responsible for the total alkalinity of the ocean. The chemical reactions in the ocean include photosynthesis and respiration, which remove or add CO<sub>2</sub>, respectively. The charges remain constant even though the forms of carbon change.

Alkalinity defined by the conservative ion budget equals the alkalinity defined by the proton acceptor/donor budget. The proton acceptor/donor budget definition of the total alkalinity is the number of moles of H+ ions equivalent to the excess of proton acceptors over proton donors in one kg of sample. Bases formed from acids with pK>=4.5 are proton acceptors, while acids with pK<4.5 are considered proton donors.

Electroneutrality is the property where the sum of the positive charges of the cations equals the sum of the negative charges of the anions. The mass budget of conservative cations and conservative anions can be computed as a charge. To maintain electroneutrality, the sum of the positive charges must equal the sum of the negative charges.



Figure 8: Carbonate species as they comprise DIC (left) and total alkalinity (right) across a range of pH.

$$[Na^{+}] + 2 * [Mg^{2+}] + 2 * [Ca^{2+}] + [K^{+}] + [H^{+}]$$

$$- [Cl^{-}] - 2 * [SO_{4}^{2-}] - [NO_{3}^{-}] - [HCO_{3}^{-}] - 2 * [CO_{3}^{2-}] - [B(OH)_{4}^{-}] - [OH^{-}] = 0$$
(45)

This equation can also be expressed as  $z_j[c_j]=0$  where  $[c_j]$  is concentration of a compound,  $z_j$  is the charge of the compound, and j is the compound.

An important principle arises here, namely that the charge balance of water itself is zero, whereas TA is positive. What accounts for the charge imbalance? It turns out that TA is also the charge imbalance of conserved cations (positively charges) over conserved anions (negative charges). Conserved in this context means that they don't vary with temperature or pressure, nor are they proton donors or acceptors at the pH threshold of 4.5 used in the definition of TA above. Thus, an alternative expression for total alkalinity is by way of these conserved species:

$$TA = [Na^{+}] + 2 [Mg^{2+}] + 2 [Ca^{2+}] + [K^{+}] + \dots +$$

$$- [Cl^{-}] - 2 [SO_{4}^{2-}] - [NO_{3}^{-}]$$
(46)

The importance of this expression is that it relates a change in TA by way of a conserved cation, such as  $[Mg^{2+}]$  or  $[Ca^{2+}]$  originating from mineral dissolution, to a change in TA that includes carbonate terms, i.e.  $[HCO_3^{--}]$  and  $[CO_3^{2-}]$ . The sum of total charges remain constant even while the forms of DIC change. Below, we will develop an expression for this change, dDIC/dTA, which quantifies a "stoichiometry" between cations and carbonate species, based on the fundamental equations provided above.

The complexity of the stoichiometry is due to the presence of both monovalent  $[HCO_3^{-1}]$  and divalent  $[CO_3^{2^-}]$ , which causes the stocihiometric ration to value between 1:2 (two  $[HCO_3^{-1}]$  per  $[Mg^{2^+}]$  or  $[Ca^{2^+}]$ ) at lower pH down to 1:1 (one  $[CO_3^{2^-}]$  per divalent cation) at higher pH. Moreover, the original dissolution event will likely take place in an environment (i.e. soil) that is more acidic, not saline, and at a different temperature, than the ultimate sink for cations and carbonates (i.e. the ocean), which is less acidic, very saline, and differs by temperature. Because the dissolution constants of carbonic acid vary with temperature and salinity, and the distribution of carbonates between  $[HCO_3^{-1}]$  and  $[CO_3^{2^-}]$  varies with acidity, the answer is not straigtforward. Nonetheless, we will arrive at an analytical expression for dDIC/dTA that can be used in terrestrial, riverine, and marine environments. We will show that the stoichiometry at the source is what can be measured and verified as the site of sequestration; that the stoichiometry at the ocean sink is what will be stored on millenial timescales; and the difference between these two can be interpreted as leakage of  $[CO_2]$  back into the atmosphere.

First, simplify the expressions for DIC and TA to be functions of  $[CO_2]$  and  $[H^+]$  alone. For convenience (and consistency with Zeebe [?]) we'll use notation where  $s = [CO_2]$  and  $h = [H^+]$ .

From (3.1) express  $[OH^-]$  as:

$$[OH^{-}] = \frac{K_{w}}{h} \tag{47}$$

From (3.5) express  $[HCO_3^-]$  as:

$$[\text{HCO}_3^{-}] = s \cdot \frac{K_1}{h} \tag{48}$$

From (3.5) and (3.6) express  $[CO_3^{2^-}]$  as:

$$[CO_3^{-}] = s \cdot \frac{K_1 K_2}{h^2} \tag{49}$$

These allow us to express DIC and TA as:

$$DIC = s \cdot \left[1 + \frac{K_1}{h} + \frac{K_1 K_2}{h^2}\right] \tag{50}$$

$$TA = s \cdot \frac{K_1}{h} + s \cdot 2 \cdot \frac{K_1 K_2}{h^2} + \frac{K_w}{h} - h$$
(51)

With these definitions in place, we can develop an estimate of dDIC/dTA. First, compute the derivative dTA/dh:

$$\frac{dTA}{dh} = -s \cdot \left(\frac{K_1}{h^2} + 4 \cdot \frac{K_1 K_2}{h^3}\right) - \frac{K_w}{h^2} - 1$$
(52)

Next compute the derivative *dDIC/dh*:

$$\frac{dDIC}{dh} = -s \cdot \left(\frac{K_1}{h^2} + 2 \cdot \frac{K_1 K_2}{h^3}\right) \tag{53}$$

Finally multiply *dDIC/dh* by the inverse of *dTA/dh* to calculate *dDIC/dTA*:

$$\frac{dDIC}{dTA} = \frac{dDIC}{dh} \cdot \frac{dh}{dTA}$$
(54)

What these calculations show is that (at constant temperature and salinity) at lower pH values, the C storage per cation introduced is higher than the C storage per cation at higher pH. At pH 5.5, the change in DIC per change in TA is nearly 1:1, though at higher pH such as 8.3 the balance is lower because some of the charge is balanced by  $CO_3^{2-}$ , not just HCO3<sup>-</sup> (Figure 9a). At lower pH, the change in pH is also more significant per unit TA than at higher pH (Figure 9b).



Figure 9: Change in derivatives of carbonate system with respect to changes induced by a change in alkalinity. Derivatives of DIC (left) and pH (right).

Additionally, these calculations can illustrate the impact of alkalinity on pH, which surfaces the counter-intuitive phenomenon that alkalinity is not simply the inverse of acidity.

$$\frac{dpH}{dTA} = -\log_{10}(e) \cdot \frac{1}{h} \cdot \frac{dh}{dTA}$$
(55)

Figure 9 shows that across any value of pH, additions in alkalinity always result in positive increases in pH and thus reductions in acidity.

In the ocean, dissolved boric acid contributes to the alkalinity budget. Total boron, that is the sum of  $B(OH)_3$  and  $B(0H)_4^-$ , is proportional to salinity, which itself varies with the freshwater budget, both influx of freshwater from rivers, and evaporation of pure water from the surface.

The constant for boric acid is defined as:

$$K_{\rm B} = \frac{[{\rm H}^+][{\rm B}({\rm OH})_4^-]}{[{\rm B}({\rm OH})_3]}$$
(56)

It is computed as:

$$\ln K_B = \left(-8966.9 - 2890.53S^{1/2} - 77.942S + 1.728S^{3/2} - 0.0996S^2\right) / T$$

$$+ 148.0248 + 137.1942S^{1/2} + 1.62142S$$

$$- \left(24.4344 + 25.085S^{1/2} + 0.2474S\right) \ln T + 0.053105S^{1/2}T$$
(57)

In marine settings (where S is large and pH > 8), the boric acid term  $(\frac{K_B B_T}{K_B + h})$  is added to the equation for TA, and the derivative of TA with respect to h becomes:

$$\frac{dTA}{dh} = -s \cdot \left(\frac{K_1}{h^2} + 4 \cdot \frac{K_1 K_2}{h^3}\right) - \frac{K_B B_T}{K_B + h^2} - \frac{K_w}{h^2} - 1$$
(58)

In the ocean, the alkalinity is more or less defined by the consistent cation/anion budget, proportional to salinity. Alkalinity measures the charge concentration of anions and cations in the solutions, and is equal to the number of moles of acid (e.g. HCl) to add to neutralize the anions of the weak acid equals the carbonate alkalinity. The carbonate system is one contributor to total alkalinity, though there are other contributors including boric acid  $(B(OH)_4^-)$ , phosphoric acid, and water. Practical alkalinity (pA) is a simplified equation for alkalinity, which includes carbonate alkalinity, borate alkalinity, and water alkalinity, following the equation:

$$pA = [HCO_3^-] + 2 * [CO_3^{2-}] + [B(OH_4)^-] + [OH^-] - [H^+]$$
(59)

The equilibrium constants in the carbonate equations depend on pressure and temperature, which vary throughout the water column. Thus, as carbon sinks from the surface to deeper waters, these values change. However, when only the temperature and pressure change (and not salinity), DIC and TA are constant.

Ocean alkalinity is roughly -2.5. As pH increases, with no other changes to the system, carbonate alkalinity will decrease (Figure 10).

#### **D.0.1 Aqueous Carbonate System Chemistry**

Dissolved inorganic carbon (DIC) in natural water is made up of three components: free  $CO_2$  (a gas), the bicarbonate ion ( $HCO_3$ ), and the carbonate ion ( $CO_3^2$ ). The relative abundance of these carbon compounds is a major driver of water pH. Free  $CO_2$  is the dominant acid, while the two carbonates contribute to the alkalinity. The amount of exchange of water surface  $CO_2$  with the atmosphere depends on the carbonate equilibrium state of the water, defined by water pH and alkalinity, along with temperature and salinity among others. Oceanic pH and alkalinity (TA) sit in a narrow range and hence so does oceanic DIC, sitting around 2400 $\mu$ M. River water has a greater variation in alkalinity, which leads to a greater range of DIC: from <20 $\mu$ M to 5000 $\mu$ M in acidic and alkaline waters respectively.

With fixed pCO<sub>2</sub>, an increase in pH (decline in [H+]) results in an increase of DIC and TA (Fig. 11). Soil pH can be as low as 5.5, and ocean pH is typically 8.3. As pH increases, total DIC and



Figure 10: This figure shows carbonate alkalinity vs. pH. The dashed lines show where pH=8.3, and carbonate alkalinity = -2.5.

the fraction of DIC that is bicarbonate increases. Across these pHs, total TA is primarily due to bicarbonate ( $HCO_3$ ), though as pH increases carbonate ( $CO_3^2$ ) accounts for a larger proportion. Aqueous CO<sub>2</sub> never changes, as it is set by the atmosphere and the solubility constant of CO<sub>2</sub>. However, declines of [H+] push the equation to the right, bringing especially more HCO3- into the solution.

Due to the chemical equilibrium relationship between water surface  $CO_2$  and atmospheric  $CO_2$ , a variation in water alkalinity drives a change in the amount of DIC stored. We refer to the carbon storage potential of the water as the DRI, which is defined as dDIC/dTA, the variation in the DIC caused by a small change in alkalinity. At constant temperature and salinity, across that range of pH, all increases in TA (e.g. by the introduction of a conservative cation) must be balanced by an increase of DIC and must be balanced by an increase in pH. However, while the balance is initially 1:1 of conservative cation to DIC (e.g.  $Mg^{2+}:HCO_3$ ), the balance drops to approx 0.85 at pH 8.3, because some of the charge is balanced by  $CO_3^2$ . The amount of change in DIC and pH induced by a change in TA varies according to pH - as seen in Fig. 12).

As pH increases from soil to the ocean, the change in DIC per unit of TA decreases from about 1 to 0.85. The change in pH per unit of TA also decreases, from 0.09 to nearly 0. These decreases occur because as pH increases, more of the alkalinity charge is balanced by carbonate ( $CO_3^2$ ) rather than bicarbonate ( $HCO_3$ ).

When considering about the long-term storage of  $CO_2$  removed on the field through enhanced weathering, the oceanic DRI acts as a limiting factor on the amount of carbon that can be stored. In order to ensure we are not overestimating the amount of carbon removed through the application of silicate rocks, we need to validate that there is no leakage in the river, over and above the expected oceanic leakage. Additional leakage would occur if the river DRI dropped below oceanic DRI,



Figure 11: Changes in DIC and TA driven by pH.

which could potentially happen due to the greater variation in river alkalinity. DRI is conventionally defined between 0, when variation in alkalinity does not affect the DRI, and 1, when a change in alkalinity corresponds to an equal change in DRI.

Solving the marine carbonate system is done in python with PyCO2SYS [?]. Note that any two core parameters (including but not limited to DIC, TA, partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>), plus auxiliary data including temperature, pressure, and salinity, are enough to solve for the complete carbonate equilibrium [?].

DRI is defined as the change in DIC (dDIC) per change in TA (dTA), as in the equation:

$$DRI = \frac{dDIC}{dTA} = \frac{dDIC}{dh} \cdot \frac{dh}{dTA}$$
(60)

which are calculated as

$$\frac{dDIC}{dh} = -s \cdot \left(\frac{K_1}{h^2} + 2 \cdot \frac{K_1 K_2}{h^3}\right) \tag{61}$$

and

$$\frac{dTA}{dh} = -s \cdot \left(\frac{K_1}{h^2} + 4 \cdot \frac{K_1 K_2}{h^3}\right) - \frac{K_w}{h^2} - 1 \tag{62}$$

where h are the protons and  $K_x$  are kinetic rate constants. The full derivation can be found in Appendix D.

We note that our derivation of DRI takes a different form but align in results with the alkalinization carbon-capture efficiency (ACCE) derived in [?].



Figure 12: Changes in dDIC/dTA and dpH/dTA driven by pH.