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Carbon Capture Efficiency of Natural Water Alkalinization

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Alkalinization of natural waters by the dissolution of natural or artificial minerals is a promising solution to sequester atmospheric CO$_2$ and counteract acidification. Here we address the alkalinization carbon capture efficiency (ACCE) by deriving an analytical factor that quantifies the increase in dissolved inorganic carbon in the water due to variations in alkalinity. We show that ACCE strongly depends on the water pH, with a sharp transition from minimum to maximum in a narrow interval of pH values. We also compare ACCE in surface freshwater and seawater and discuss potential bounds for ACCE in the soil water. Finally, we present two applications of ACCE. The first is a local application to 156 lakes in an acid-sensitive region, highlighting the great sensitivity of ACCE to the lake pH. The second is a global application to the surface ocean, revealing a latitudinal pattern of ACCE driven by differences in temperature and salinity.

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Carbon-Capture Efficiency of Natural Water Alkalinization

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Abstract
Alkalinization of natural waters by the dissolution of natural or artificial minerals is a promising solution to sequester atmospheric CO_2 and counteract acidification. Here we address the alkalinization carbon-capture efficiency (ACCE) by deriving an analytical factor that quantifies the increase in dissolved inorganic carbon in the water due to variations in alkalinity. We show that ACCE strongly depends on the water pH, with a sharp transition from minimum to maximum in a narrow interval of pH values. We also compare ACCE in surface freshwater and seawater and discuss potential bounds for ACCE in the soil water. Finally, we present two applications of ACCE. The first is a local application to 156 lakes in an acid-sensitive region, highlighting the great sensitivity of ACCE to the lake pH. The second is a global application to the surface ocean, revealing a latitudinal pattern of ACCE driven by differences in temperature and salinity.

Scientific Significance Statement
The rising levels of atmospheric CO_2 are increasing the global temperatures and acidifying the ocean at unprecedented rates. A promising solution that could mitigate both trends relies on increasing water alkalinity by the dissolution of natural or artificial minerals. It is known that when the minerals dissolve, they counteract water acidification and promote a transfer of CO_2 from the atmosphere to the water. However, it is currently unknown how to quantify the CO_2 captured in the water per unit of mineral dissolved. We here address this issue by deriving an analytical factor that quantifies the carbon-capture efficiency of mineral dissolution as a function of the water chemistry. We discuss the implications for carbon capture in natural waters, and we present applications to the lakes of an acid-sensitive region and the ocean.

Keywords
Carbon capture — Alkalinity — Freshwater — Ocean — Ehnanced Weathering — Analytical Factor

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Introduction and Motivation

To limit global warming, several strategies to sequester atmospheric CO_2 are being developed [1, 2]. Among these, increasing the alkalinity, i.e., alkalinization, of natural waters has the potential to sequester large quantity of atmospheric CO_2 and mitigate the acidification of the ocean and surface freshwaters [3, 4]. Alkalinization can be achieved through dissolution of natural minerals or artificial materials that preferably contain important biological macronutrients as calcium (Ca) and magnesium (Mg) [3, 5, 6].

To accelerate the weathering (i.e., the dissolution) of natural minerals, these have to be finely ground and spread in environments where the mineral dissolution and the consequent carbon-capture might be favored (e.g., ocean coasts or wet soils) [3, 7]. This technique, referred to as Ehnanched Weathering (EW), has been gaining attention as a promising geoengineering solution with large potential for CO_2 removal and limited technological requirement [3, 5, 8, 9, 10].

As these minerals dissolve, the water alkalinity increases, promoting a transfer of CO_2 from the atmosphere to the water in the form of aqueous carbonates (e.g., HCO_3^-), according to the well known reactions

$$CaCO_3 + CO_2 \downarrow + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad (1)$$

$$CaSiO_3 + 2\,CO_2 \downarrow + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Si(OH)_4, \quad (2)$$

where calcium carbonate ($CaCO_3$) and wollastonite ($CaSiO_3$) can be more generally interpreted as any carbonate and silicate mineral or rock. From the reactions (1) - (2), it is evident that silicate minerals offer a greater carbon-capture potential compared to carbonate minerals, as they do not have already stored-in-rock carbon.

Due to the great variety of chemical conditions of natural waters, reactions (1) - (2) are not always representative of the mineral dissolution. In the presence of a strong acid (e.g., HNO_3 commonly found in acid rains and fertilized catch-

ments), the dissolution reactions read

$$CaCO_3 + 2HNO_3 \rightarrow Ca^{2+} + 2NO_3^- + H_2O + CO_2 \uparrow, \quad (3)$$

$$CaSiO_3 + 2HNO_3 + H_2O \rightarrow Ca^{2+} + 2NO_3^- + Si(OH)_4, \quad (4)$$

Hence the carbon-capture efficiency of the mineral is strongly hampered and, as in the case of carbonate in (3), the dissolution may even become a CO_2 source to the atmosphere.

The reduction in the amount of CO_2 captured implied by (3) and (4) obviously represents a loss of efficiency of mineral dissolution. While it has long been recognized [3, 11], however, the impact of such a loss of efficiency has not been objectively quantified. In particular, for the purposes of assessing and comparing the effectiveness of natural climate solutions, it would be highly desirable to have a quantitative parameterization of the carbon-capture efficiency of such reactions as a function of the chemical condition of the water solution, both at the site of dissolution and along the hydrologic pathway where the mineral dissolution cations are transported.

With this in mind, and with the broad goal of improving the reliability of carbon-sequestration estimated via EW, we here derive an analytical factor that quantifies the increase in the Dissolved Inorganic Carbon (DIC) in the water solution in response to variations in water alkalinity (Alk). This fundamental measure of efficiency is here referred to as Alkalinization Carbon-Capture Efficiency (ACCE). It further enables an exact definition of the alkalinization carbon-capture efficiency of any mineral, in turn indicated as ACCEM, that quantifies the amount of CO_2 captured per molecule of mineral dissolved.

We show that ACCE is mainly driven by the water pH and, to a lesser extent, by the concentration of CO_2 in the air. By accounting for the effects of temperature and salinity, we also present analogies and differences for ACCE in freshwater and seawater. We conclude with two applications of ACCE: a local application to freshwater lakes in an acid-sensitive region, and a global application to the surface ocean, which plays the main role in the CO_2 sequestration pathway via water alkalinization.

1. Theoretical Considerations

Using the concepts of Dissolved Inorganic Carbon (DIC) and alkalinity (Alk), in this Section we derive the general expression of the alkalinization carbon-capture efficiency (ACCE). We also obtain a specific form of ACCE for any mineral (ACCEM). Due to the slow mineral dissolution, we consider equilibrium conditions of the chemical species in the water. We only review here the necessary definition and refer to [12, 13, 14] for more details on the basic background.

Dissolved Inorganic Carbon (DIC). The dissolved inorganic carbon is defined as

$$[DIC] = [HCO_3^-] + [CO_3^{2-}] + [CO_2], \quad (5)$$

where $[CO_2]$ is the sum of carbon dioxide in aqueous form $[CO_2(aq)]$ ($> 99.5\%$) and the true undissociated carbonic acid $[H_2CO_3]$ ($< 0.5\%$) [13]. Square brackets indicate molar concentration (M). At equilibrium, $[CO_2]$ is related to the partial pressure of carbon dioxide in the air phase (p_{CO_2}) through Henry's law

$$[CO_2] = K_H p_{CO_2}, \quad (6)$$

where K_H is Henry's solubility constant (M/atm). Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions arise from the reactions

$$CO_2 + H_2O \overset{K_1}{\rightleftharpoons} H^+ + HCO_3^- \overset{K_2}{\rightleftharpoons} 2H^+ + CO_3^{2-}, \quad (7)$$

$$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^-, \quad (8)$$

where (8) is water dissociation, and K's are equilibrium constants. All quantities in the aqueous carbonate system above can be expressed analytically in terms of only two components; choosing p_{CO_2} and pH ($pH = -Log[H^+]$) as independent variables, one can write

$$[HCO_3^-] = K_1 K_H p_{CO_2} / [H^+], \quad (9)$$

$$[CO_3^{2-}] = K_1 K_2 K_H p_{CO_2} / [H^+]^2, \quad (10)$$

$$[OH^-] = K_w / [H^+]. \quad (11)$$

The concentrations of the aqueous carbonate species as a function of pH are shown in Fig. 1 for a surface freshwater in equilibrium with the atmosphere.

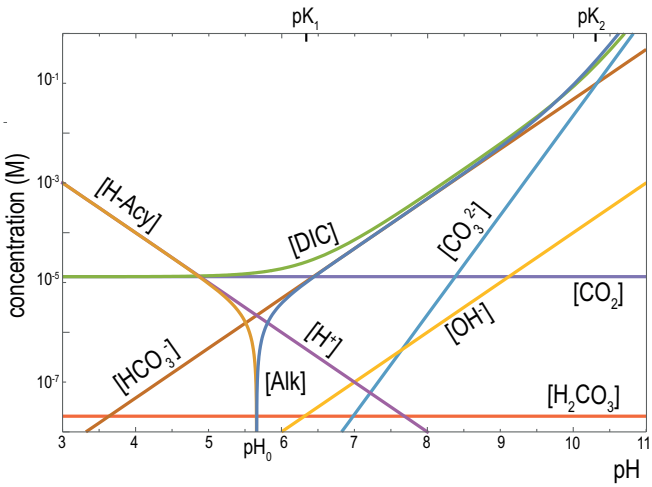


Figure 1. Alkalinity [Alk] and mineral acidity [H-Acy] of the aqueous carbonate system as a function of pH for a surface freshwater in equilibrium with the atmosphere ($pCO_2 = 4 \cdot 10^{-4}$ atm). Equilibrium constants are evaluated after [13] for standard condition.

Alkalinity. Alkalinity expresses the proton deficiency of the aqueous solution with respect to a reference proton level, which is conventionally defined by the CO_2-equivalence point [14, 15]. Hence, the alkalinity involves the non-conservative

ions that can accept (e.g., HCO_3^-) or donate (e.g., H^+) protons and represents the acid-neutralizing capacity of an aqueous system. Since in most cases weak acids or bases other than aqueous carbonates (and borates for the case of ocean) can be neglected, the alkalinity definition reads [13, 14]

$$[\mathrm{Alk}] = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}], \tag{12}$$

expressed in equivalents per liter (M_{eq}). Borate speciation is reported in the Appendix. When there is a proton excess with respect to the equivalence point (i.e., $[\mathrm{Alk}]<0$), the water is acidic and the proton excess is given by the mineral acidity $[\mathrm{H-Acy}]$, i.e., $[\mathrm{H-Acy}] = -[\mathrm{Alk}]$ [13]. The pH of transition between acidic ($[\mathrm{H-Acy}]>0$) and alkaline ($[\mathrm{Alk}]>0$) conditions is a function of the p_{CO_2} and, for a surface freshwater in equilibrium with the atmosphere, reads $pH_0 \sim 5.6$ (Fig. 1).

Alkalinity can also be expressed in terms only of species that are conservative to changes in pressure, temperature, and pH, by combining Eq. (12) and the zero-charge balance [14, 15] as

$$[\mathrm{Alk}] = \sum \mathrm{cc} - \sum \mathrm{ca}, \tag{13}$$

where $\sum$cc and $\sum$ca are the sum of equivalent conservative cations (i.e., $\sum \mathrm{cc} = 2[\mathrm{Ca^{2+}}] + 2[\mathrm{Mg^{2+}}] + [\mathrm{K^+}] + [\mathrm{Na^+}] + \ldots$) and anions (i.e., $\sum \mathrm{ca} = 2[\mathrm{SO_4^{2-}}] + 2[\mathrm{NO_3^{2-}}] + [\mathrm{Cl}]^- + \ldots$) in the aqueous solution, respectively. The impact of changes in cation concentration on the alkalinity becomes much clearer with this alternative definition. For example, it is immediately evident from Eq. (13) that an addition of Ca^{2+} to the water solution from the dissolution of a molar unit of $CaCO_3$ or $CaSiO_3$ increases water alkalinity by 2 molar units as Ca^{2+} enters in $\sum$cc. Drawing the same conclusion from (12) would not be as easy, because an addition of $CaCO_3$ affects the water pH and hence the concentration of all the non-conservative species of the aqueous carbonate system.

ACCE derivation. The previous considerations allow us to define formally the Alkalinization Carbon Capture Efficiency (ACCE) as the variation of [DIC] due to a small change in [Alk] (e.g., by dissolution of alkaline minerals). Specifically, as both [DIC] and [Alk] are known as a function of pH

$$\begin{aligned}
[\mathrm{DIC}] &= K_\mathrm{H} p_{CO_2} \left(1 + \frac{K_1}{[\mathrm{H^+}]} + \frac{K_1 K_2}{[\mathrm{H^+}]^2}\right), \\
[\mathrm{Alk}] &= \frac{K_1 K_\mathrm{H} p_{CO_2}}{[\mathrm{H^+}]} + \frac{2 K_1 K_2 K_\mathrm{H} p_{CO_2}}{[\mathrm{H^+}]^2} + \ldots \\
&\quad \ldots \frac{[\mathrm{B_T}] K_B}{[\mathrm{H^+}] + K_B} + \frac{K_w}{[\mathrm{H^+}]} - [\mathrm{H^+}],
\end{aligned}$$

we can evaluate their differential with respect to a variation in $[\mathrm{H^+}]$ (constant p_{CO_2}) as

$$d[\mathrm{DIC}] = \frac{\partial[\mathrm{DIC}]}{\partial[\mathrm{H^+}]} d[\mathrm{H^+}], \quad d[\mathrm{Alk}] = \frac{\partial[\mathrm{Alk}]}{\partial[\mathrm{H^+}]} d[\mathrm{H^+}], \tag{14}$$

where $\partial\cdot/\partial\cdot$ indicates partial differentiation. Further taking the ratio of the two differentials yields the sought measure of efficiency

$$\mathrm{ACCE} = \frac{d[\mathrm{DIC}]}{d[\mathrm{Alk}]} = \frac{\beta p_{CO_2}([\mathrm{H^+}] + 2K_2)}{\alpha p_{CO_2} + [\mathrm{H^+}](\beta p_{CO_2} + K_W) + [\mathrm{H^+}]^3 (1 + f_B)}, \tag{15}$$

where $\alpha = 4K_1K_2K_\mathrm{H}$, $\beta = K_1K_\mathrm{H}$, and f_B is a term indicating the influence of the borates (see Appendix). Thus, by quantifying the variation of [DIC] due to a small change in [Alk], ACCE provides an objective measure of the sensitivity of the concentration of inorganic carbon in water to alkalinity. Importantly, its definition is valid for any biogeochemical process that affects the water alkalinity (e.g., mineral dissolution or precipitation, nutrients uptake by biota, etc.). Moreover, ACCE being defined between 0 and 1, it conveniently spans the range of conditions from zero, when the alkalinity variation does not affect the amount of DIC in the water, to one, when the alkalinity increment corresponds to an equal increment of DIC.

This new measure of carbon-capture efficiency adds to the list of factors in the literature, which are obtained as the ratio of differentials of two variables of the water-air system (e.g., the well-known Revelle factor, which is the ratio of the differentials of p_{CO_2} and DIC [16]). These factors are of extreme interest to oceanographers and climate change scientists as they serve as rigorous tools to evaluate the response of the ocean chemistry to natural and human-induced changes [17, 18]. Similarly, the ACCE factor derived here enables a quantification of the increase in inorganic carbon that follows water alkalinization.

ACCE of a Mineral (ACCEM). Based on the previous general definition of carbon-capture efficiency, we can also define the alkalinization carbon-capture efficiency of a given mineral or material (ACCEM) as the CO_2 captured in the aqueous solution per molecule of mineral dissolved. In formula,

$$\mathrm{ACCEM}_m = n_m \mathrm{ACCE} - \mathrm{C}_m, \tag{16}$$

where the subscript m indicates that the parameter depends on the alkaline mineral, or material, considered (see Table 1); C_m is the number of carbon atoms contained in the mineral molecule; and n_m is the increase in alkalinity caused by a molar increment in the amount of dissolved mineral, which can be conveniently evaluated through the definition (13) of alkalinity, as previously explained.

2. Results

In this Section we explore the influences of the two governing parameters, pH and p_{CO_2}, on the alkalinization carbon capture efficiency (ACCE) obtained in the previous section.

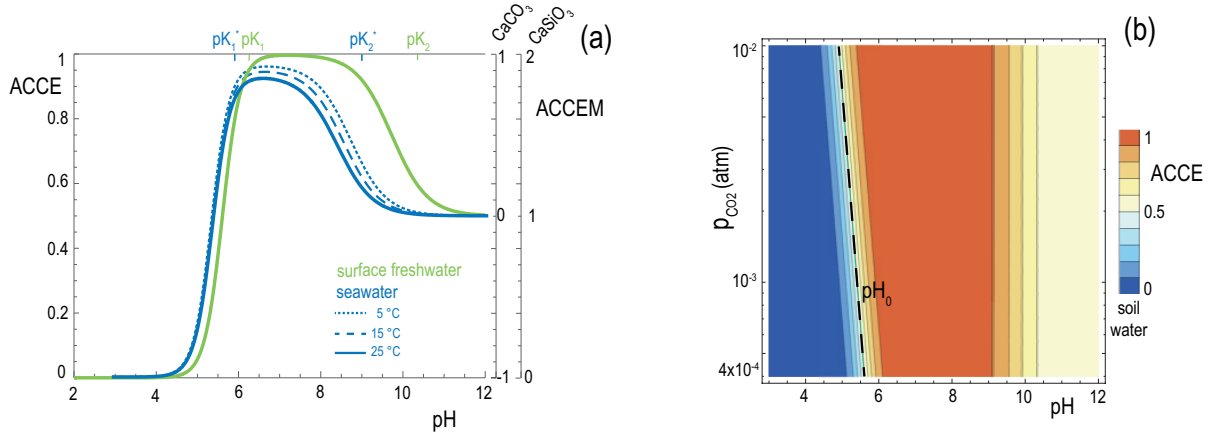


Figure 2. ACCE as a function of the water chemistry. (a) ACCE, and ACCEM for $CaCO_3$ and $CaSiO_3$, as a function of pH for freshwater (green) and seawater (light blue) in equilibrium with the atmosphere ($p_{CO_2} = 4 \cdot 10^{-4}$ atm). Temperature effect for freshwater is negligible (not shown). pK_1, pK_2 and pK_1^*, pK_2^* are the dissociation constants of carbonic acid for freshwater [13] and seawater [14], respectively (labelled in the upper axis for $T = 25°$and average ocean salinity). (b) Contour plot of the factor ACCE in the plane $\{pH, p_{CO_2}\}$ for a soil freshwater. This is an upper bound for ACCE (see text). The black dashed line (pH_0) separates alkaline and acidic waters (i.e., [Alk]=0).

Table 1. ACCEM and related parameters for some common natural minerals and artificial materials. ACCEM is reported as [minimum, maximum].

Mineral	n	C	ACCEM
$CaSiO_3$	2	0	[0,2]
Mg_2SiO_4, Fe_2SiO_4	4	0	[0,4]
$CaCO_3, MgCO_3$	2	1	[-1,1]
$CaMg(CO_3)_2$	4	2	[-2,2]
$Ca(OH)_2, Mg(OH)_2$	2	0	[0,2]
CaO, MgO	2	0	[0,2]

Influence of pH. The factor ACCE from Eq. (15) and, consequently, also the ACCEM for the different minerals, strongly depend on the water pH. In particular, as shown in Fig. 2a, ACCE undergoes a sharp transition between values close to zero and a maximum (ACCE$\approx$1 or freshwater and ACCE$\approx$ 0.9 for seawater) in the pH range 4.5 to 6.5, i.e., in the transition between alkaline and acidic waters (see Fig. 1).

ACCE is basically zero for pH<4.5, namely in acidic water, where an increase in alkalinity – or more properly a decrease in mineral-acidity – does not affect the amount of DIC in the water. Indeed, at these pH's, the carbonate ions (HCO_3^- and CO_3^{2-}) do not form (Fig. 1). On the contrary, ACCE is maximized when the increase in alkalinity is associated with an increment in the concentration of bicarbonate ions HCO_3^- (i.e., for pH$>pK_1$). This maximum of ACCE is rather flat and forms a plateau, which is broader for freshwater than seawater. At even higher pH, ACCE decays again to $\approx$0.5 (at pH$>pK_2$) as bicarbonates (HCO_3^-) are substituted by carbonates (CO_3^{2-}).

Even though the trend of ACCE is qualitatively similar for seawater and freshwater, there are substantial quantitative differences. Regarding the maximum of ACCE, while in freshwater the variation in alkalinity may be completely associated with the carbonate buffer (max of ACCE$\approx$ 1), in seawater the variation in alkalinity is partially associated with the borate buffer (max of ACCE<1). This effect is stronger at higher temperatures because the CO_2 solubility decreases and the ratio of total borates (conservative to temperature variation) to DIC (non-conservative) increases.

The difference in the plateau width of the maximum of ACCE is instead due to the different dissociation constants for carbonic acid in freshwater pK_1, pK_2, i.e., thermodynamic constants in the approximation of diluted waters, and seawater pK_1^*, pK_2^*, i.e., stoichiometric constants accounting for salinity. Specifically, since $pK_2^* < pK_2$, which indicates that seawater has a much higher concentration of CO_3^{2-} than freshwater at the same pH, the decay of ACCE from the plateau occurs at lower pH values for seawater. This is an important factor in reducing the carbon-capture efficiency in the ocean and provides a detailed justification and analytical quantification of the loss of efficiency in seawater, already pointed out by [8, 19].

Influence of p_{CO_2} and Implications for EW in Soils. Beside the pH, the other parameter affecting ACCE is the p_{CO_2}, i.e., the concentration of CO_2 in the air. Some of the largest ranges of pCO_2 are found in soils, where due to biotic respiration, pCO_2 can be much higher than the typical atmospheric values. For this reason, soil have been considered as a convenient environment for enhanced weathering (EW)[3, 5].

Fig. 2b shows a 2D plot of ACCE as a function of pH and p_{CO_2}. The p_{CO_2} weakly affects the pH region of transition between the ACCE minimum and maximum, which is around the transition between alkaline and acidic waters, i.e., the CO_2-equivalence point pH_0. To an increase in p_{CO_2} there

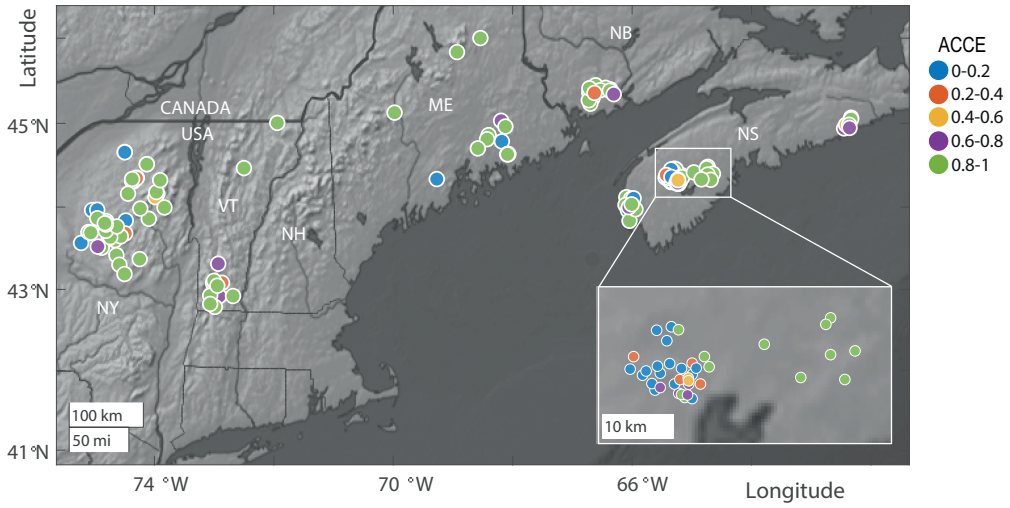


Figure 3. Evaluation of ACCE for 156 lakes in the acid-sensitive Atlantic region between the USA and Canada. pH values (2010-2017 averaged) have been obtained from the Long-Term Monitoring (LTM) EPA program for US lakes [20] and the Acid Sensitive Lakes Study for the Canada Lakes [21]. Long-term equilibrium with the atmosphere has been assumed, $p_{CO_2} = 4 \cdot 10^{-4}$ atm.

corresponds a shift in the lower limit of the pH interval where ACCE is maximized.

The above results suggest that the soil is a very efficient environment for EW (also recalling that acid soils would favor the weathering rates). However, it is important to stress that ACCE actually represents an upper bound for real soil conditions, as it does not account for several other buffer mechanisms – besides those related to carbonates – that commonly characterize the soil environment (e.g., cation exchange with colloids, organic matter, and non-negligible presence of other weak acids and bases [27]). The combined effect of these buffers could reduce the actual value of EW efficiency in a manner which is similar to that of borates in the oceans (Fig. 2a). Further research will be devoted to this issue.

3. Applications

The factor ACCE can be used to quantify the carbon-capture efficiency due to natural or artificially enhanced mineral weathering in a variety of natural waters. As the spreading of finely ground minerals is a worldwide practice to counteract local acidifications of agricultural soils or surface freshwaters [11, 28], the range of possible ACCE applications spans from the local scale (e.g., the agricultural field) to the global scale (e.g., refining the estimates of EW potential as a geoengineering technology).

With this perspective, we here provide two applications of ACCE: a local application to freshwater lakes in an acid-sensitive region, which could benefit from an EW treatment, and a global application to the surface ocean, which plays the main role in the CO_2 sequestration pathway via water alkalinization.

Acid Sensitive Lakes. It is well known that past industrial emissions of sulfates and nitrates have caused acidification of surface freshwater in several regions of the World, especially in Northern Europe and North America [29]. Dispersion of finely ground alkaline minerals (mostly $CaCO_3$) has often been used as a countermeasure [28].

In the American Northern Atlantic coast, freshwater lakes have not recovered from past natural (i.e., organic acids) and anthropic (i.e., acid rains) acidification [21], and could benefit from EW application (some trial applications have been performed [30]). To get a better sense of the potential of this solution, we calculated ACCE for 156 lakes in this region. Since we do not consider the organic buffer of the lakes, the ACCE presented here should be considered as an upper bound.

The results, shown in Fig. 3, clearly indicate how the different lake pH's drive the carbon-capture efficiency, following the trend in Fig. 2a. In the lakes with lower pH, the increase in alkalinity due to mineral cations does not promote any carbon-capture in the lake water ($ACCE \approx 0$). This points to a tradeoff, in acidic waters, between counteracting acidification and carbon-capture efficiency.

The fact that $ACCE \approx 0$ also implies that if carbonate minerals were used (e.g., $CaCO_3$), there would be a loss of carbon towards the atmosphere as $ACCEM_{CaCO_3} = -1$ from eq. (16). Thus, to the purpose of climate mitigation, non-carbonate minerals should be preferred.

Global Surface Ocean. It is estimated that currently the ocean is absorbing around a third of the anthropogenic CO_2 emissions and, as a consequence, its average pH has lowered of around 0.1 since preindustrial times, with serious concerns for marine biology [31, 32]. Alkalinization of the ocean by mineral dissolution would counteract such trend and, at the

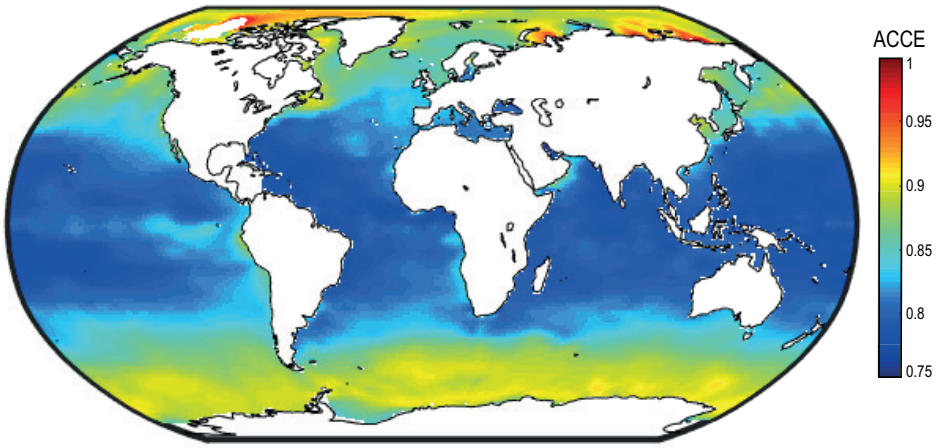


Figure 4. Map of ACCE in the surface ocean (30 m). Climatology data of DIC and Alk (1°x 1°), which have been converted to pCO_2 and pH through CO2SYM software [22], are from the GLODAP project [23, 24]; temperature and salinity data (2005-2017 averaged) are from the World Ocean Atlas [25, 26].

same time, stably sequester atmospheric CO_2 at geological timescales ($\sim$ 1000 kyr) [4]. For example, local injections of alkalinity are being evaluated as a way to protect the Great Barrier Reef from acidification [33].

As mentioned earlier, due to the ocean chemistry and in particular to the relatively high ratio of carbonate to bicarbonates, there is a reduction of carbon-capture efficiency for the mineral cations in seawater, i.e., for the average ocean pH $\approx$8.1, ACCE $\approx$0.8 at standard conditions (see Fig.2a). To further investigate this effect, we calculated the global distribution of ACCE in the surface ocean.

The results, shown in Fig. 4, reveal a latitudinal trend for ACCE that is induced by differences in temperature and salinity. In particular, colder and fresher waters in arctic and antarctic latitudes favor the carbon-capture efficiency (ACCE$\approx$0.9), compared to warmer and saltier waters in tropical and temperate latitudes (ACCE$\approx$0.8). This difference in efficiency results from the combined effects of higher CO_2 solubility at lower temperatures, and lower ratio of carbonate to bicarbonates in fresher waters (i.e., higher value of pK_2^*). Because the mineral dissolution is favored by high temperatures [3], the ACCE$\approx$0.8 of tropical and temperate latitudes can be used as a reference for most practical applications.

4. Conclusion

Increasing the alkalinity of natural waters, in particular of the ocean, is a promising strategy to mitigate climate change and water acidification. Here we have provided a mathematical expression for the quantification of the alkalinization carbon-capture efficiency (ACCE) as a function of the water chemistry. The spectrum of applications covers any soluble alkaline mineral or material (ACCEM) in a variety of natural waters.

The results have demonstrated that ACCE strongly depends on the water pH (Fig. 2). In particular, ACCE is minimum in strongly acidic waters (pH<4.5), and is maximum in alkaline waters where the formation of HCO_3^- is favored ($pK_1 < pH \ll pK_2$). In the sharp transition from minimum to maximum, ACCE is very sensitive to the water pH, e.g., the variation of a freshwater pH from 5 to 6 changes the ACCE from 0.05 to 0.85. A practical consequence is that counteracting acidification through mineral dissolution may promote very different results in terms of carbon capture in the freshwater lakes of a same region (Fig. 3).

In seawater, the efficiency is generally lower than in surface freshwaters, for the same pH, due to the presence of the borates and the relatively higher concentration of CO_3^{2-} (Fig. 2a). Furthermore, the application of ACCE to the global surface ocean (Fig. 4) has revealed that, due to differences in temperature and salinity, the carbon-capture efficiency is lower in tropical and temperate latitudes (ACCE$\approx$0.8) than in polar latitudes (ACCE$\approx$0.9).

Regarding EW in soils, high values of p_{CO_2} increase the pH interval where ACCE is maximized (Fig. 2b) supporting the idea that soils are a very convenient environment for carbon-capture. However, more research is needed to quantify the possible losses of efficiency due to the non-negligible presence of other buffers (e.g., organic matter and cation exchange with colloids). Additional analyses should also address the temporal dynamics of carbon-capture efficiency of the mineral cations as they are transported by the hydrological cycle.

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A. Borates

The borate buffer plays an important role in ocean alkalinity. Boric acid dissociates as

$$\mathrm{B(OH)_3 + H_2O \overset{K_B}{\rightleftharpoons} B(OH)_4^- + H^+}, \tag{17}$$

where K_B is the stochiometric dissociation constant, evaluated after [14]. The equilibrium concentrations of the two borate species as a function of pH read

$$\mathrm{B(OH)_3} = \frac{[\mathrm{H^+}]}{[\mathrm{H^+}]+K_B}[\mathrm{B_T}], \tag{18}$$

$$\mathrm{B(OH)_4^-} = \frac{K_B}{[\mathrm{H^+}]+K_B}[\mathrm{B_T}]. \tag{19}$$

where $[\mathrm{B_T}]$ is the total boron concentration, which is related to salinity (S) through $[\mathrm{B_T}] = 4.16 \cdot 10^{-4} S/35$ (M) [14]. The contributions of borate to ACCE for seawater in eq. (15) reads

$$f_B = \frac{K_B}{([\mathrm{H^+}]+K_B)^2}[\mathrm{B_T}]. \tag{20}$$

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