



# Large and active CO<sub>2</sub> uptake by coupled carbonate weathering

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## ABSTRACT

Carbonate mineral weathering coupled with aquatic photosynthesis on the continents, herein termed *coupled carbonate weathering* (CCW), represents a current atmospheric CO<sub>2</sub> sink of about 0.5 Pg C/a. Because silicate mineral weathering has been considered the primary geological CO<sub>2</sub> sink, CCW's role in the present carbon cycle has been neglected. However, CCW may be helping to offset anthropogenic atmospheric CO<sub>2</sub> increases as carbonate minerals weather more rapidly than silicates. Here we provide an overview of atmospheric CO<sub>2</sub> uptake by CCW and its impact on global carbon cycling. This overview shows that CCW is linked to climate and land-use change through changes in the water cycle and water-born carbon fluxes. Projections of future changes in carbon cycling should therefore include CCW as linked to the global water cycle and land-use change.

## 1. Introduction

A critical question in the science of global climate change is how to balance the atmospheric CO<sub>2</sub> budget (Broecker et al., 1979; Tans et al., 1990; Melnikov and O'Neill, 2006; Houghton, 2007; Ciais et al., 2013). According to Ciais et al. (2013), a large terrestrial carbon sink is missing from the global carbon cycle (C<sub>missing</sub>) as follows:

$$C_{\text{missing}} = \text{sources} - \text{sinks} = (\text{emissions from fossil fuels} \\ + \text{net emissions from changes in land use}) \\ - (\text{oceanic uptake} + \text{atmospheric increase}) \quad (1)$$

where the current estimates in Pg C/a (1 Pg = 10<sup>15</sup> g) are

$$2.5 = 9.2 - 6.7 = (8.3 + 0.9) - (2.4 + 4.3) \quad (2)$$

Locations, magnitudes, variations and mechanisms responsible for the terrestrial missing carbon sink, however, are uncertain. Prevailing models focus on carbon sinks in soil and vegetation whereby the missing carbon sink reflects enhanced primary production from elevated atmospheric CO<sub>2</sub> concentrations and/or nitrogen fertilization (Hudson et al., 1994; Friedlingstein et al., 1995; Kheshgi et al., 1996; Pan et al., 2011; Arneeth et al., 2017). For example, Kheshgi et al. (1996) found that ~25% of CO<sub>2</sub> emissions are sequestered by the terrestrial biosphere. Pan et al. (2011) estimated a net global forest sink of

1.1 ± 0.8 Pg C/a, or about 1 Pg C/a smaller sink than needed to balance Eq. (2). The missing sink may simply result from uncertainties of sources and sinks in the mass balance estimate. However, these uncertainties, particularly of the terrestrial sink, may be the major complications in projections of future perturbations in the cycle and thus carbon sink mechanisms, variability, and magnitudes must be better understood to predict responses of the global carbon cycle to increased atmospheric CO<sub>2</sub> concentrations (Houghton, 2007). One such carbon sink could be carbonate mineral weathering, which we evaluate here as a potential sink for atmospheric CO<sub>2</sub> at short timescales (years – millennia) and could thus react to rapid perturbations of the global carbon cycle.

Models of atmospheric CO<sub>2</sub> have considered how the global carbon cycle reacts to enhanced chemical weathering of silicate rocks with warming caused by increased atmospheric CO<sub>2</sub> (Berner, 2004). However, slow silicate weathering rates mean this effect operates over longer timescales than expected from anthropogenic atmospheric CO<sub>2</sub> increases (Berner et al., 1983; Berner, 2003; Sabine et al., 2004; Ciais et al., 2013). For example, in current models of the global carbon cycle (Ciais et al., 2013), four major carbon reservoirs may be perturbed at timescales of years to centuries: the atmosphere, oceans, terrestrial ecosystems, and fossil fuels. Terrestrial ecosystem fluxes can be evaluated by riverine carbon fluxes, which are commonly assumed to

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remain unchanged following increased atmospheric CO<sub>2</sub> concentration from anthropogenic sources (Sabine et al., 2004; Ciais et al., 2013). At timescales longer than millennia, processes such as silicate mineral weathering and volcanism dominate the global carbon cycle (Berner et al., 1983; Berner, 2004). However, these processes exchange only small amounts of carbon annually (< 0.3 Pg/a) and are generally ignored in C budgets over time periods shorter than a century or so (Sabine et al., 2004; Ciais et al., 2013).

Silicate weathering impacts carbon cycling by converting atmospheric CO<sub>2</sub> to bicarbonate that is transported to the ocean, then precipitated and buried as solid carbonate minerals (Berner et al., 1983). In contrast, CO<sub>2</sub> consumed by carbonate mineral weathering is offset by a CO<sub>2</sub> source from marine carbonate mineral precipitation (Berner et al., 1983; Berner, 2003, 2004). However, carbonate rocks weather more rapidly than silicate rocks, and, as shown below, control dissolved inorganic carbon (DIC) concentrations in almost all catchments (Liu et al., 2011). These elevated DIC concentrations may also enhance aquatic photosynthetic uptake of DIC (Liu et al., 2010b, 2011; Yang et al., 2016; Chen et al., 2017). If the produced organic carbon (OC) is buried in sediments, it would be removed from short-term carbon cycling as long-term storage similar to the marine biological carbon pump (Longhurst and Harrison, 1989; Ma et al., 2014). We define the links between carbonate mineral weathering and aquatic photosynthesis as *coupled carbonate weathering* (CCW) and suggest this process may previously have been underestimated by a factor of about 3, amounting to ~0.5 Pg C/a on land (Liu et al., 2010b, 2011). This result indicates that silicate weathering may represent only 6% of the uptake of atmospheric CO<sub>2</sub> with the remaining 94% from carbonate mineral weathering (Liu et al., 2011). Therefore, atmospheric CO<sub>2</sub> uptake by CCW may be significant in controlling both short- and long-term climate changes (Liu et al., 2011), so that weathering of Ca-rich silicate rocks alone may not dominate long-term climate change (Berner et al., 1983; Berner, 2003, 2004).

Here, we show, by synthesizing findings in rock-weathering research and studies of the biological carbon pump effects in surface water systems, that the carbon uptake by CCW totals ~0.5 Pg C/a on land (Liu et al., 2010b, 2011), comparable with that in the world's forests (Pan et al., 2011) and displays a significant increasing trend under the dual influence of global climate and land-use changes. Therefore, atmospheric CO<sub>2</sub> uptake by CCW should be included in the global carbon budget, at least over the relatively short time-scales relevant to human activities.

## 2. Dominance of carbonate mineral weathering in silicate watershed DIC production

Although primarily occurring in carbonate rocks, carbonate minerals (mainly calcite, aragonite and dolomite) can be disseminated as minor components within silicate rocks (Blum et al., 1998). Therefore, the CO<sub>2</sub> consumed in silicate rock terrains, which is commonly estimated based on DIC concentrations of streams, can result primarily from weathering of the secondary carbonate rather than primary silicate minerals (Blum et al., 1998; White et al., 1999; Jacobson et al., 2002a, 2002b, 2003; Oliver et al., 2003; White et al., 2005; Moore et al., 2013; Jacobson et al., 2015). This dominance of carbonate over silicate minerals results from estimated weathering rates that are ~350 times faster than plagioclase (Jacobson et al., 2003). The discussion below evaluates carbonate mineral weathering's role in silicate terrains related to glaciation and tectonic uplift in the Himalayas, New Zealand and Iceland.

Uplift of the Himalaya-Tibetan Plateau has been proposed to have stimulated CO<sub>2</sub> consumption by silicate rock weathering and led to Cenozoic cooling (Edmond, 1992; Raymo and Ruddiman, 1992). However, although the bedrock contains only ~1% carbonates, around 82% of the HCO<sub>3</sub><sup>-</sup> flux was derived from dissolution of carbonate minerals with the remaining 18% from silicate mineral weathering (Blum

et al., 1998). This carbonate weathering would contribute elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios, causing the Cenozoic increase in oceanic Sr isotope ratios. In addition, high <sup>87</sup>Sr/<sup>86</sup>Sr ratios (up to 0.93–1.11) in dolomite occur within most Himalayan tributaries of the Ganges and Brahmaputra rivers and complicate their use as a tracer of silicate weathering (Oliver et al., 2003). Thus, models of changing oceanic <sup>87</sup>Sr/<sup>86</sup>Sr ratios through time are likely to have overestimated the amount of CO<sub>2</sub> consumption by silicates (Blum et al., 1998). Overestimation of CO<sub>2</sub> drawdown by Himalayan silicate weathering may also result from conventional application of two-component Ca/Sr and <sup>87</sup>Sr/<sup>86</sup>Sr mixing equations (Jacobson et al., 2002a). This effect results from (1) a wide range of Ca/Sr and <sup>87</sup>Sr/<sup>86</sup>Sr ratios in the Himalayas that are ill-defined by a single end-member in conventional mass-balance equations and (2) precipitation of Ca<sup>2+</sup> in calcite during transport in Himalayan stream waters that drives dissolved Ca<sup>2+</sup>/Sr<sup>2+</sup> ratios toward values lower than those of the carbonate bedrock (Jacobson et al., 2002b).

That carbonate weathering is faster than silicate, even for trace carbonate minerals in silicate terrains, is shown by variations in magnitudes of carbonate weathering following exposure of rock surfaces. Carbonate mineral dissolution was estimated to provide > 90% of the weathering-derived HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> for at least 55 ka following initial exposure of glaciated rock surfaces in a silicate-dominated, Himalayan catchment, although carbonates represent only ~1.0 wt% of the fresh glacial till (Jacobson et al., 2002a). Therefore, stream water Ca<sup>2+</sup>/Sr<sup>2+</sup> and <sup>87</sup>Sr/<sup>86</sup>Sr ratios, and hence HCO<sub>3</sub><sup>-</sup> concentrations, can be erroneously interpreted to represent predominately silicate dissolution (Gaillardet et al., 1999). These problems may explain why high estimates of CO<sub>2</sub> consumption from silicate mineral weathering have been proposed (Gaillardet et al., 1999) despite the fact that silicate weathering rates are several orders of magnitude lower than those of carbonates (Dreybrodt, 1988; White and Brantley, 2003).

Calcium isotopes indicate that riverine Ca<sup>2+</sup> in the Southern Alps of New Zealand largely originates from carbonate mineral weathering although the bedrock contains only ~3% calcite (Moore et al., 2013). The magnitude of carbonate weathering in rapidly uplifted areas (~90%) was about twice that of slowly uplifted areas (~50%–60%) reflecting the more rapid kinetics of carbonate than silicate weathering. This tectonic relationship was corroborated by elemental and Sr isotope geochemistry of stream waters, bedload sediment, and hydrothermal calcite veins, and attributed to the tectonic exhumation and mechanical denudation of metamorphic bedrock (Jacobson et al., 2003). Using these findings, Moore et al. (2013) suggested that atmospheric CO<sub>2</sub> consumption by silicate weathering in glacial watersheds experiencing the highest uplift rates accounts for < 1% of the global CO<sub>2</sub> consumption flux, again suggesting silicate weathering during Himalayan uplift could be smaller than previously estimated (Edmond, 1992; Raymo and Ruddiman, 1992). These studies suggest that rapid mountain uplift results in an enhanced influence of carbonate mineral weathering on the dissolved ions delivered to seawater.

Freshly deposited basalt weathering, for example following volcanism in Iceland, has been implicated in long-term CO<sub>2</sub> drawdown and climate regulation (Gaillardet et al., 1999). However, Ca isotopes of Icelandic surface and ground waters showed that calcite weathering provides 0–65% of the Ca<sup>2+</sup> in non-glacial rivers and 25–90% of the Ca<sup>2+</sup> in glacial rivers, with silicate rock weathering providing the remainder (Jacobson et al., 2015). These results suggest that basalt weathering may be less significant in global carbon cycling than previously proposed (Gaillardet et al., 1999). These findings, along with similar findings in recently exposed glacial terrains and uplifted areas, reflect the important contribution of carbonate mineral weathering to the consumption of atmospheric CO<sub>2</sub> and that previous studies (Berner et al., 1983; Gaillardet et al., 1999) may have overestimated the importance of silicate rock terrains. These studies, even though they relate to long-term CO<sub>2</sub> drawdown, demonstrate that even in silicate terrains, the carbonate minerals may dominate the weathering reactions, particularly during early stages of weathering.

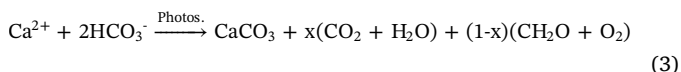
### 3. Sensitivity of carbonate mineral weathering to climate and land-use change

In the worst case anthropogenic emission scenario, atmospheric CO<sub>2</sub> concentration is predicted to double before the end of the twenty-first century (Ciais et al., 2013), resulting in a global warming of > 6 °C and changes in the hydrologic cycle through shifting rainfall patterns and continental vegetation cover (Wentz et al., 2007). These changes should impact chemical weathering of rocks (Probst et al., 1994; Jacobson et al., 2003; Raymond and Cole, 2003; Tipper et al., 2006; Ford and Williams, 2007; Macpherson et al., 2008; Raymond et al., 2008; Liu et al., 2010b; Beaulieu et al., 2012; Jeannin et al., 2016; Zeng et al., 2016a, 2016b). For example, atmospheric CO<sub>2</sub> doubling is expected to increase CO<sub>2</sub> weathering consumption by > 50% in the Mackenzie River Basin (Beaulieu et al., 2012) even though atmospheric CO<sub>2</sub> consumption by weathering has been considered to be at a steady-state since the industrial revolution (Sabine et al., 2004; Ciais et al., 2013). However, recent work has demonstrated sensitivity of weathering and CO<sub>2</sub> consumption to ongoing climate and land-use change. The flux of CO<sub>2</sub> into the atmosphere from China's Yangtze River, for example, decreased by ~75% during the four decades between ~1960–2000 due to a marked increase in nutrient (e.g. NO<sub>3</sub><sup>-</sup>) concentrations and fertilization for phototroph growth which lowered the pCO<sub>2</sub> of the river water (Wang et al., 2007).

We propose that short-term weathering, dominated by carbonate rocks, may play a more important role in the evolution of the global carbon cycle than previously recognized over the coming centuries. The magnitudes of atmospheric and soil CO<sub>2</sub> consumed by weathering were estimated to be 3720 and 600 kg C/km<sup>2</sup>/a for the Amazon and the Congo basins, respectively, i.e., about a 6-fold difference (Probst et al., 1994). Similarly, CO<sub>2</sub> consumed by rock weathering has increased by 10% and 0.7% for the Amazon and Congo Basins, respectively, over the past century. These differences relate to the proportion of carbonate rocks in each basin. ~49% of the Congo Basin is underlain by silicate rocks, 42% by crystalline and metamorphic rocks, and only 9% by carbonate rocks. The Amazon Basin has greater geologic diversity and greater exposure of carbonate rock (Probst et al., 1994). Consequently, the greater increase in CO<sub>2</sub> consumption of the Amazon Basin than the Congo Basin over the last century appears to reflect differences in carbonate rock contents. The relationship between CO<sub>2</sub> consumption and carbonate mineral contents may also depend on land-use change in carbon pools and fluxes within the basins. This dependence would be related to primary productivity within basins which could be linked to inorganic carbon contents of the watersheds (Zeng et al., 2017).

### 4. Photosynthetic uptake of DIC by aquatic phototrophs

DIC (the sum of CO<sub>2</sub>(aq), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>, which occurs mainly as HCO<sub>3</sub><sup>-</sup> at 6.5 < pH < 10) in surface water systems, is consumed by aquatic phototrophs on the continents and in the ocean (Invers et al., 2001; Kahara and Vermaat, 2003; Cassar et al., 2004; Iglesias-Rodriguez et al., 2008; Pedersen et al., 2013; Liu et al., 2015; Yang et al., 2015; Noges et al., 2016; Yang et al., 2016; Chen et al., 2017; Liu et al., 2017):



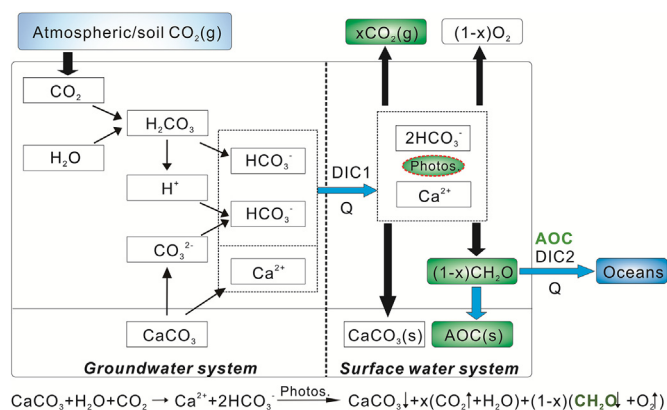
which occurs throughout surface water systems, including rivers, lakes, wetlands, reservoirs, and the oceans. The production of CO<sub>2</sub> (second term on right of Reaction 3) will elevate the pCO<sub>2</sub> of the water, typically causing some C to outgas to the atmosphere. The third term on the right shows the production of OC, which plays an important role in the carbon cycle by means of the so-called biological carbon pump (BCP) (Longhurst and Harrison, 1989; Sarmiento, 1993; Passow and Carlson, 2012; Sanders et al., 2014; Hain et al., 2014; Liu et al., 2015; Yang

et al., 2016; Chen et al., 2017). This process occurs when phototrophs transform DIC in the water to OC, lowering pCO<sub>2</sub>. No net change occurs in the water pCO<sub>2</sub> if the produced OC is remineralized to CO<sub>2</sub> before burial. However, burial of the OC represents a net loss of atmospheric CO<sub>2</sub> to the lithosphere (Liu et al., 2011). The oceanic BCP is estimated to keep the concentration of CO<sub>2</sub> in air to approximately 30% of what it would be in its absence (Sarmiento, 1993).

Our argument that CCW is an important atmospheric CO<sub>2</sub> sink results from the continuous uptake of DIC by phototrophs that produce OC, both in the oceans and in continental aquatic ecosystems (Ternon et al., 2000; Einsele et al., 2001; Jones et al., 2003; Lerman and Mackenzie, 2005; Flanagan et al., 2006; Yang et al., 2008; Liu et al., 2015; Yang et al., 2015; Maavara et al., 2017). Lerman and Mackenzie (2005) found that primary production and net storage of OC reduces the CO<sub>2</sub> released by carbonate precipitation in marine systems, leading to lower CO<sub>2</sub> emissions from the surface layer through reaction 3. A terrestrial impact on the marine BCP occurs as fertilization of the outflow plume of the Amazon River lowers pCO<sub>2</sub> (Ternon et al., 2000). In purely terrestrial settings, modern lake basins bury about 0.07 Pg C/a of atmospheric carbon. This mass is more than a quarter of the annual atmospheric carbon burial in the modern oceans, although the aggregate surface area of the world's lakes is only about 0.8% of the ocean surface (Einsele et al., 2001). Illustrating this important lacustrine carbon sink, the carbon emission from a subtropical, eutrophic lake was only about 8% of the carbon burial (Yang et al., 2008). Extensive lacustrine OC burial occurs because lakes are characterized by rapid sediment accumulation resulting in a preservation factor on average 50 times greater than that observed in the oceans (Einsele et al., 2001). Negative relationships between sedimentation rate and water pCO<sub>2</sub> support the potential significance of photosynthetic uptake of DIC by aquatic phototrophs in the carbon cycle (Flanagan et al., 2006). Heathcote and Downing (2012) showed impacts of eutrophication on carbon burial in freshwater lakes in an intensively agricultural landscape in the US state of Iowa which has watersheds that have been heavily modified over the last 150 years. Their results show increasing carbon burial for all lakes as agriculture intensified. In nearly all the cases, burial rates increased to very high levels up to 200 g C m<sup>-2</sup>y<sup>-1</sup> following agricultural development. These results support the idea that the increased autochthonous and allochthonous carbon flux, related to anthropogenic change, leads to higher rates of carbon burial. Further, these results imply that the fraction of global carbon buried by lakes will be increasingly important in the future if worldwide trends in anthropogenic eutrophication continue. In a more recent study Pacheco et al. (2014), developed carbon budgets of highly eutrophic lakes. Their analyses show that lakes undergoing eutrophication can become atmospheric CO<sub>2</sub> sinks because of the CO<sub>2</sub> disequilibrium caused by extreme primary production. Carbon budgets of such lakes show they absorb both landscape and atmospheric carbon, converting it into lake sediments and passing additional DOC downstream. Therefore, eutrophication may cause a reversal in the role played by oligotrophic lakes by promoting atmospheric carbon sequestration as sediment and DOC. This means that as eutrophication increases from agriculture and urbanization, the expected large CO<sub>2</sub> evasion to the atmosphere by natural lakes will decline substantially and inland carbon sequestration and enrichment of DOC in waters flowing to the sea will be augmented.

### 5. Large CO<sub>2</sub> uptake by coupled carbonate weathering

In an attempt to balance the atmospheric CO<sub>2</sub> budget, we (Liu et al., 2010b) previously considered the effect by CCW (Fig. 1) and found the CO<sub>2</sub> sink by this mechanism could be as large as ~0.5 Pg C/a on land. This sink was calculated as DIC<sub>r</sub> + AOC<sub>r</sub> + AOC<sub>(s)t</sub>, where DIC<sub>r</sub> is the dissolved inorganic carbon flux from the rivers to the ocean and AOC<sub>r</sub> is the autochthonous organic carbon (formed within the aquatic ecosystem by transformation of DIC to AOC via aquatic photosynthesis) flux from rivers to the ocean, and the sedimentary AOC flux in surface

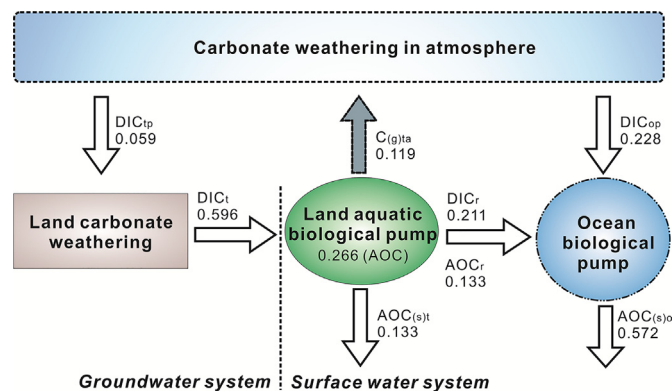


**Fig. 1.** Conceptual model of atmospheric/soil  $\text{CO}_2$  uptake by coupled carbonate weathering (drawing in reference to Liu et al. (2010b, 2011)). Notes: 1. CSF (Carbon Sink Flux produced by CCW) =  $Q \times (0.5[\text{DIC}_2] + [\text{AOC}]) / A + F_{\text{AOC}(\text{s})}$ , where:  $Q$  is the discharge from the surface water system; the ratio 0.5 indicates that only one half of the  $\text{HCO}_3^-$  generated by carbonate mineral dissolution is of atmospheric origin;  $[\text{DIC}_2]$  is the concentration of DIC (Dissolved Inorganic Carbon) in the surface water system;  $[\text{AOC}]$  is the concentration of AOC (Autochthonous Organic Carbon) in the surface water system transformed from  $\text{DIC}_1$  (DIC in the groundwater system) by submerged aquatic phototrophs via photosynthesis in the surface water system; and  $F_{\text{AOC}(\text{s})}$  is the sedimentary flux of AOC in the surface water systems over the watershed area ( $A$ ). 2. Unlike the conventional carbonate mineral weathering carbon cycle model (Bernier et al., 1983) ( $x = 1$  in the chemical reaction at bottom of the figure), which considers carbonate- $\text{H}_2\text{O}$ - $\text{CO}_2$  interaction and ignores AOC production by aquatic photosynthetic uptake of DIC (Photos. = photosynthesis by autotrophs), this new conceptual model ( $0 \leq x < 1$ ) helps to answer important questions such as whether CCW could be contributing to the long-term carbon sink (e.g., through sedimentation, burial of AOC), and thus, to a proportionate degree, controlling long-term climate change.

water systems on land is  $\text{AOC}_{(\text{s})\text{t}}$  (Fig. 2). This estimate of the  $\text{CO}_2$  sink accounts for ~50% of the net terrestrial missing carbon sink and is comparable to the carbon sink in the world's forests (Pan et al., 2011). This value is more than three times larger than the estimate of 0.14 Pg C/a obtained by a previous study (Gaillardet et al., 1999). By neglecting the photosynthetic uptake of DIC by terrestrial aquatic phototrophs and burial of part of the resulting AOC on the continents ( $\text{AOC}_r + \text{AOC}_{(\text{s})\text{t}} = 0.27$  Pg C/a, Fig. 2) previous studies underestimated the carbonate mineral weathering  $\text{CO}_2$  uptake. This value is reflected in local estimates from the Mississippi River system (the largest in North America) where 20% to 57% of the total organic carbon (TOC) consists of the AOC (Waterson and Canuel, 2008). Similar percentages of AOC (~65%) were found in China's second largest river, the Pearl River (Yang et al., 2016). If the lower estimate, 20%, is multiplied by the sedimentary deposition of OC in inland waters (0.6 Pg C/a) plus riverine TOC discharge to oceans (0.5 Pg C/a) (Battin et al., 2009), then 0.22 Pg C/a of AOC is obtained, similar to the estimate above (0.27 Pg C/a). These estimates suggest that atmospheric  $\text{CO}_2$  uptake by CCW on continents may have previously been significantly underestimated.

## 6. Increase in $\text{CO}_2$ uptake due to climate and land-use change

A substantial amount of the atmospheric  $\text{CO}_2$  taken up on land through photosynthesis and chemical weathering is transported laterally from upland terrestrial ecosystems to the ocean (Gaillardet et al., 1999; Cole et al., 2007; Battin et al., 2009). These global carbon budget estimates commonly assume the carbon transport has remained unchanged since pre-industrial times (Sabine et al., 2004; Ciais et al., 2013), although human activities appear to have altered these fluxes (Raymond and Cole, 2003; Raymond et al., 2008; Regnier et al., 2013). Anthropogenic perturbations have enhanced carbon export from soils, thereby increasing the flux to inland waters by as much as 1.0 Pg C/a



**Fig. 2.** Atmospheric carbon sources and sinks (Pg C/a) by coupled carbonate weathering (redrawing in reference to Liu et al. (2010b, 2011)). DIC: Dissolved Inorganic Carbon; AOC: Autochthonous Organic Carbon;  $\text{DIC}_{\text{tp}}$ : Carbon sink resulting from precipitation in the ocean;  $\text{DIC}_{\text{op}}$ : Carbon sink resulting from precipitation in the ocean;  $\text{DIC}_l$ : Carbonate mineral weathering carbon flux on the land;  $\text{C}_{(\text{g})\text{ta}}$ : Carbon source flux from waters on the land;  $\text{DIC}_r$ : DIC flux from rivers to the ocean;  $\text{AOC}_r$ : AOC flux from rivers to the ocean;  $\text{AOC}_{(\text{s})\text{t}}$ : AOC sedimentary flux in surface water systems on land ( $0.133 = 0.266 \times 50\%$ , i.e., assuming that half of the AOC was buried in terrestrial surface water system (Battin et al., 2009));  $\text{AOC}_{(\text{s})\text{o}}$ : AOC sedimentary flux in the ocean. We attribute DIC and  $\text{AOC}_r$  to short-term terms, while  $\text{AOC}_{(\text{s})\text{t}}$  and  $\text{AOC}_{(\text{s})\text{o}}$  may constitute long-term carbon sink by burial of AOC. Note: (1) The conventional carbon cycle model of carbonate mineral weathering (Bernier et al., 1983) does not consider organic processes, i.e.  $x = 1$  in the CCW reaction (Fig. 1), and all  $\text{CO}_2$  gas is returned to the atmosphere. Thus the carbonate mineral weathering does not form a net long-term carbon sink, and cannot influence climate change over extended timescales. The present CCW model took  $x = 0.2$ , the mean release ratio of  $\text{CO}_2$  from the surface water system to the atmosphere (with large variations from 2% to 30%, Liu et al., 2010b), a net long-term carbon sink ( $\text{AOC}_{(\text{s})\text{t}} + \text{AOC}_{(\text{s})\text{o}} = 0.705$  Pg C/a) was derived, and may influence long-term climate change. (2) To fix the values of  $\text{AOC}_r$  and  $\text{AOC}_{(\text{s})\text{t}}$  is more difficult because we are lack of systematic investigation of AOC formed by the biological carbon pump in the global terrestrial aquatic ecosystems. Therefore, more work is needed on this issue in future.

since pre-industrial times (Regnier et al., 2013). Most of this additional carbon input into upstream rivers is either emitted back into the atmosphere as carbon dioxide (~0.4 Pg C/a) or sequestered in sediments (~0.5 Pg C/a), leaving a net input of ~0.1 Pg C/a to the open ocean, which should be included in global C budgets (Regnier et al., 2013).

Such assessments (Cole et al., 2007; Battin et al., 2009; Regnier et al., 2013), however, do not show the detailed mechanisms controlling these changes. As shown in Figs. 1 and 2, atmospheric/soil  $\text{CO}_2$  uptake by CCW has three components:  $\text{DIC}_r$ ,  $\text{AOC}_r$ , and  $\text{AOC}_{(\text{s})\text{t}}$ . This  $\text{CO}_2$  uptake may increase with changes in the global hydrologic cycle as a consequence of global warming, rising anthropogenic emissions of  $\text{CO}_2$ , and reforestation, which may increase the soil  $\text{pCO}_2$  and thus rates of carbonate rock dissolution (Liu et al., 2010b). In addition, fertilization with nutrients such as N, P, C, Fe, Zn, and Si may increase organic matter storage/burial by aquatic phototrophs and thus decrease the  $\text{CO}_2$  returning to the atmosphere. Based on the ensemble mean projection of global climate change for the year 2100 by the IPCC, it is estimated that the atmospheric  $\text{CO}_2$  uptake will increase by 21%, or about 0.18 Pg C/a (Liu et al., 2010b). However, the uncertainty in the estimation of this uptake points to a need for further field investigations.

### 6.1. Increase in DIC fluxes in relation to increasing atmospheric/soil $\text{CO}_2$ and land-use

Recent studies indicate that the DIC flux by CCW (corresponding to  $\text{DIC}_r$  in Fig. 2) may be increasing in relation to increasing atmospheric/soil  $\text{CO}_2$  and land-use.

Groundwater CO<sub>2</sub> increased by 20% between 1991 and 2005 at Konza Prairie, Kansas (Macpherson et al., 2008), an undisturbed mid-continental North American grassland underlain by carbonate minerals. This preserved prairie lacks complexities of changing land use and water management that are problematic in large-river chemistry research in developed countries. The long-term increase was greater than the 7% increase in atmospheric CO<sub>2</sub> recorded over the same time period and resulted from increased soil CO<sub>2</sub> from the microbial breakdown of vegetation and/or root respiration. The latter two factors may be synergistically enhanced in relation to increasing atmospheric CO<sub>2</sub> (Andrews and Schlesinger, 2001; King et al., 2004; Wan et al., 2007), and/or increasing atmospheric temperatures (Wan et al., 2007). Therefore, groundwater at the site represents a CO<sub>2</sub> sink through limestone weathering, as soil-generated CO<sub>2</sub> is transformed to bicarbonate. In contrast, changes in the amount and type of land cover, along with increased rainfall in the Mississippi Basin, has increased carbonate alkalinity exported from the Mississippi River by ~60% during the past half-century (Raymond and Cole, 2003). The changes in land use and management, contributed more to water and carbon exports from the Mississippi River than changes in climate and plant CO<sub>2</sub> fertilization (Raymond et al., 2008). Thus, both preserved regions and regions experiencing land use change contribute to an increasing CCW flux.

These changes have also been observed in manipulation experiments in which CO<sub>2</sub> dynamics and chemical weathering were modified in a temperate forest with the Free-Air CO<sub>2</sub> Enrichment (FACE) experiment (Andrews and Schlesinger, 2001). They found that as a result of CO<sub>2</sub> enrichment, annual soil respiration increased by 27% and was accompanied by higher CO<sub>2</sub> concentrations in the soil pore space. The increased soil CO<sub>2</sub> accelerated the rates of soil acidification and mineral weathering. They showed that an increase of 55% in atmospheric CO<sub>2</sub> concentration over 2 years resulted in a 271% increase in soil solution cation concentration, a 162% increase in alkalinity and a 25% increase in Si concentration at a depth of 200-cm. The flux of DIC to groundwater increased by 33%, such that there was a negative feedback effect.

## 6.2. Increase in DOC/TOC and OC burial fluxes in relation to climate and land-use change

The increase in riverine DOC/TOC and lake and man-made reservoir OC burial fluxes (corresponding to AOC<sub>r</sub> and AOC<sub>(s)l</sub> in Fig. 2 respectively) may be related to the increased CCW contribution in relation to climate and land-use change. There are many records of long-term increases in OC concentrations (Worrall et al., 2003; Evans et al., 2005; Vuorenmaa et al., 2006; De Wit et al., 2007) and declines in CO<sub>2</sub> supersaturation (Jones et al., 2003; Wang et al., 2007; Ran et al., 2015; Finlay et al., 2015) in the world's rivers, streams and lakes during recent decades. A roughly 100% increase in dissolved organic carbon (DOC) concentrations over 30 years occurred in the River Tees in northern England (Worrall et al., 2003). All increases in DOC or TOC were related to climate change and/or a decrease in acid deposition. However, questions remain open about the sources of DOC and/or TOC: are the DOC and/or TOC in these rivers or lakes soil-derived (*allochthonous*) or formed in aquatic ecosystems (*autochthonous*) (Bianchi et al., 2004; Bianchi et al., 2007; Yang et al., 2016)? If autochthonous, the long-term increases in OC concentrations in the world's surface water systems may also be related to fertilization by increased DIC concentrations (Iglesias-Rodriguez et al., 2008; Yang et al., 2016) if light and/or other nutrients were not limiting factors, especially under increased nutrient additions by human activities, and thus they may be linked to CCW (Liu et al., 2010b; Liu et al., 2015; Yang et al., 2015; Noges et al., 2016; Yang et al., 2016; Chen et al., 2017; Liu et al., 2017).

Increases in nutrient loading and decreases in suspended load of the Mississippi and other large rivers due to dams have resulted in significant changes in the sources and overall cycling of riverine DOC and POC. The damming of rivers is important considering autochthonous

carbon production may be a more important source of DOC and POC (Particulate Organic Carbon) than previously thought (Bianchi et al., 2004, 2007). Damming of rivers represents one of the most far-reaching human modifications of the flows of water and associated matter (Maavara et al., 2017). Upon dam closure, increased water residence time, improved light conditions, nutrient retention, and sediment trapping in the impounded reservoir can amplify primary productivity and promote the burial of autochthonous and allochthonous OC as well (Maavara et al., 2017). In-reservoir production of AOC increased by ~85% from 1970 to 2000 and the amount of OC trapped behind dams doubled over the same period (Maavara et al., 2017). Therefore, the fraction of global carbon buried by reservoirs will be increasingly important in the future if worldwide trends in anthropogenic dam construction continue.

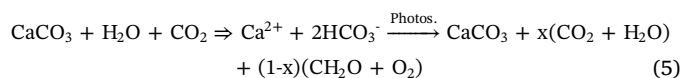
## 7. Implications of the conceptual model of coupled carbonate weathering

We have presented a model that couples the rapid kinetics of carbonate mineral dissolution and DIC production in both silicate and carbonate rock watersheds with the aquatic photosynthetic uptake of the weathering-derived DIC and subsequent burial of part of the resulting AOC (Fig. 1). Our estimates suggest that atmospheric CO<sub>2</sub> uptake by CCW may be large (Fig. 2) and may increase as global climate and land-use change. The rapidity of these reactions and sensitivity to global changes make CCW a previously underappreciated portion of the global carbon cycle that may become increasingly important as global characteristics change.

To assess the importance of CCW over geologic time, we must first evaluate the origin of carbonate minerals in the oceans and lakes since the first appearance of aquatic phototrophs about 3.416 billion years ago (Tice and Lowe, 2004). The reaction products need for carbonate precipitation could originate the silicate rock weathering reaction:

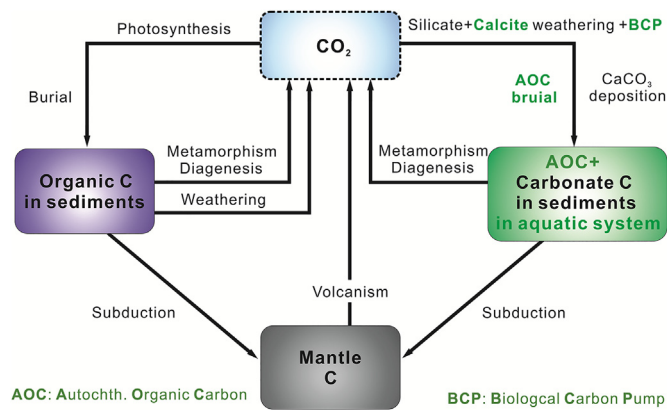


or alternatively, it could result from the CCW reaction:



We suggest that CCW (Reaction 5) dominates the sources of aquatic carbonate minerals because the kinetics of carbonate mineral weathering are several orders of magnitude faster than those of silicate mineral weathering (Liu et al., 2011).

Assuming our model estimates are correct, we need to reassess the relative contributions of both silicate and carbonate mineral weathering to the atmospheric CO<sub>2</sub> sink since the first appearance of aquatic phototrophs. Our model suggests that the atmospheric CO<sub>2</sub> sink by way of rock weathering may rest chiefly on carbonate mineral dissolution and subsequent aquatic photosynthetic uptake of the resulting DIC (Liu et al., 2011). Evidence suggests biological productivity may be enhanced or limited by the supply of DIC from rock weathering (Iglesias-Rodriguez et al., 2008; Liu et al., 2010a; Yang et al., 2016; Chen et al., 2017). DIC utilization and induced calcium carbonate precipitation by *Oocystis solitaria* Witt were higher (4.6 and 10-fold, respectively) in karst water (with high DIC concentrations, as an analogue of the carbonate aquatic ecosystem) than in non-karst water (with low DIC concentrations, as an analogue of the silicate aquatic ecosystem) (Liu et al., 2010a). Similar results occur in China's Pearl River, where phytoplankton biomass and AOC% were positively related to DIC concentration, indicating a DIC fertilization effect on aquatic photosynthesis (Yang et al., 2016). Laboratory culturing experiments showed that calcification and net primary production in the coccolithophore species *Emiliania huxleyi* are increased by high CO<sub>2</sub> partial pressures and HCO<sub>3</sub><sup>-</sup> (Iglesias-Rodriguez et al., 2008). Field evidence from the deep ocean is consistent with these laboratory conclusions, indicating that over the



**Fig. 3.** A model of the long-term carbon cycle modified from Berner (2003). The deposition of autochthonous organic carbon (AOC) from coupled carbonate weathering and silicate weathering (Biological Carbon Pump; BCP, for short) is included. The cycle can be subdivided into two subcycles involving allochthonous (soil) organic matter (left side of figure) and the rock weathering-derived carbonate and AOC deposition (right side of figure).

past 220 years there has been a 40% increase in average coccolith mass (Iglesias-Rodriguez et al., 2008). Of course, considering that inland waters are generally oversaturated in  $\text{CO}_2$  with respect to the atmosphere, aquatic primary production may be limited by other nutrients, such as P, N, Fe, or Zn, reflecting the need for further studies of the relationships between macro- and micro-nutrients and DIC fertilization.

In brief, the rock weathering-derived carbon sink may be underestimated where only DIC concentrations at river mouths are considered (Berner et al., 1983; Meybeck, 1987; Gaillardet et al., 1999), because it is necessary to consider both DIC and the transformation of DIC to AOC in rivers (Liu et al., 2010b, 2011).

The presence of a “biological carbon pump” in natural aquatic ecosystems which diverts carbon produced by Reaction 5 to the lithosphere by means of sedimentation and burial of the OC implies that CCW might also be significant in controlling long-term climate change (Hodell et al., 1999; Jarvis et al., 2011; Zhao et al., 2014; Bowen and Zachos, 2010; Ma et al., 2014), due to the substantial rates of production and burial of AOC (Fig. 3). AOC has been an important mechanism in the formation of lacustrine and marine petroleum source rocks in the past, demonstrated by periods of rapid C burial (Langrock and Stein, 2004; Zhao et al., 2014). During the Cenomanian-Turonian Oceanic Anoxic Event about 93.95 Ma ago, rising  $p\text{CO}_2$  and sea surface temperatures (SST) resulted from volcanic degassing, which led to the initiation of black shale deposits simultaneously with  $p\text{CO}_2$  and SST maxima (Jarvis et al., 2011). Black shale deposition was followed by falling atmospheric  $p\text{CO}_2$  and cooling due to carbon sequestration by marine organic productivity and preservation, the latter being related to the enhanced CCW, in addition to increased silicate mineral weathering. This finding questions the traditional point of view (Berner et al., 1983) that only chemical weathering of Ca-silicate rocks can potentially control long-term climate change by providing feedback interactions with atmospheric  $\text{CO}_2$  drawdown via precipitation of carbonate minerals. Another rapid increase in atmospheric  $\text{CO}_2$  occurred at the Paleocene–Eocene Thermal Maximum about 56 Ma ago. The rate of recovery from the  $\text{CO}_2$  increase was an order of magnitude more rapid than that expected for carbon drawdown by silicate mineral weathering alone (Bowen and Zachos, 2010). The factor causing accelerated  $\text{CO}_2$  drawdown could have been sequestration of OC (also through enhanced CCW induced aquatic organic productivity) and regrowth of carbon stocks in the biosphere or shallow lithosphere that were released at the onset of the event. These rapid drawdowns of atmospheric  $\text{CO}_2$  mainly through OC (including AOC) burial (Bowen and Zachos, 2010; Jarvis et al., 2011; Ma et al., 2014) support our new conceptual model of a net carbon uptake by CCW (Figs. 1, 3).

## 8. Conclusions and outlook

### 8.1. Conclusions

The rapid kinetics of carbonate mineral dissolution and the dominance of carbonate minerals in controlling the production of DIC in almost all watersheds, coupled with the aquatic photosynthetic uptake of weathering-derived DIC and burial of some of the resulting OC, suggest that the atmospheric  $\text{CO}_2$  uptake by CCW might be significant in controlling both short- and long-term climate changes. This questions the traditional paradigm that chemical weathering of Ca-rich silicate rocks alone controls long-term climate change.

By synthesizing findings in rock-weathering research and studies of the biological carbon pump effects in surface water systems, this review shows that the carbon uptake by CCW not only totals  $\sim 0.5$  Pg C/a on land, but may also be increasing in response to climate and land-use changes. Therefore, atmospheric  $\text{CO}_2$  uptake by CCW should be included in the global carbon budget due to both its magnitude and dynamism.

### 8.2. Outlook

Two great problems exist in the study of the carbon cycle of aquatic ecosystems: a high degree of uncertainty in estimating fluxes of carbon sources and sinks and our paucity of knowledge about the associated mechanisms. At present, oceans are considered a large carbon sink (Ciais et al., 2013) while inland waters are mainly seen as an important carbon source (Raymond et al., 2013). Although some studies (Cole et al., 2007; Battin et al., 2009) have seen inland waters as a carbon sink via the burial of OC in their aquatic ecosystems, the sources (autochthonous or allochthonous) of this OC remain to be determined. Substantial differences exist in estimates of the OC burial flux (0.2 versus 0.6 Pg C/a) (Cole et al., 2007; Battin et al., 2009). This review is therefore an effort to emphasize the importance of considering a more complete mechanism—the  $\text{H}_2\text{O}$ -carbonate- $\text{CO}_2$ -aquatic phototroph interaction in understanding the terrestrial carbon cycle.

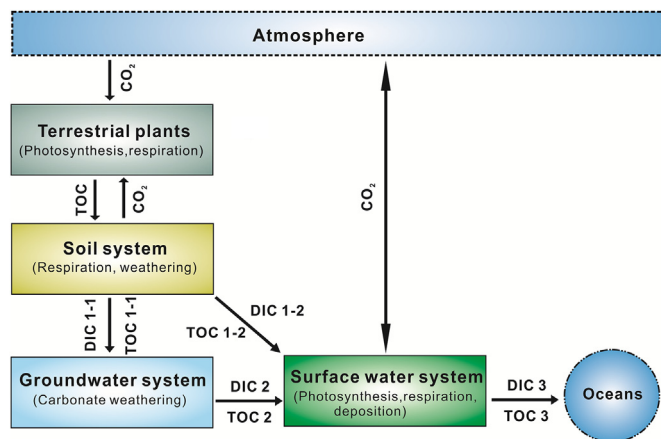
Two major processes sequester carbon on the continents (Gaillardet et al., 1999; Liu et al., 2010b; Pan et al., 2011): (1) photosynthesis of emergent plants that store the atmospheric carbon in the terrestrial ecosystem in the form of OC; and (2) CCW, during which carbon is sequestered in aquatic ecosystems as DIC and AOC. Inorganic carbon cycling is as important as organic carbon cycling but current studies of terrestrial ecosystems chiefly consider organic carbon cycling; the interaction between inorganic and organic carbon cycles has generally been neglected. Elucidating the coupled relations between the inorganic and organic carbon cycles is the key to revising the carbon cycle model, especially in extensive areas of carbonate rock.

We need to combine studies of photosynthesis and water-rock-gas interaction into a single model of water-rock (soil)-gas-organism interaction. In carbonate rock terrains, the carbon sink produced by CCW may be similar to the organic carbon sink in quantity (Liu et al., 2010b; Pan et al., 2011). Therefore, the atmosphere, vegetation, soil, carbonate and water should be considered within the context of the carbon cycle as a whole (Fig. 4).

The conventional rock weathering evaluation method based on water-rock-gas interactions considers only inorganic components; the calculation can be expressed simply as (Liu et al., 2010b):

$$\text{CSF} = F_{\text{DIC}} = n \times Q \times [\text{DIC}]/A \quad (6)$$

where CSF is the rock weathering carbon sink flux;  $F_{\text{DIC}}$  is the DIC flux via runoff;  $A$  is the watershed area;  $Q$  is the runoff discharge;  $[\text{DIC}]$  is the concentration of DIC at river mouths; and  $n$  is the rock weathering coefficient for the carbon sink. For the weathering of carbonate minerals,  $n = 0.5$  because only one half of the  $\text{HCO}_3^-$  generated by carbonate mineral dissolution ( $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ ) is of atmospheric origin. For pure silicate mineral weathering



**Fig. 4.** A model of the carbon cycle in carbonate (rock) areas based on interactions among water, rock (soil), gas, and biota. DIC: dissolved inorganic carbon; TOC: total organic carbon, including autochthonous organic carbon if present; 1–1 and 1–2: the carbon flows from soil system to groundwater system and surface water system respectively; 2 and 3: the carbon flows from groundwater system to surface water system, and from surface water system to oceans respectively.

( $\text{CaSiO}_3 + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{H}_4\text{SiO}_4$ ),  $n = 1$  because all the  $\text{HCO}_3^-$  involved is of atmospheric origin (Gaillardet et al., 1999; Liu et al., 2010b).

However, due to the presence of aquatic phototrophs, a large proportion of the DIC in aquatic ecosystems may be converted into OC (Fig. 2), forming AOC. Therefore, in order to calculate the rock weathering carbon sink flux (CSF) correctly, it is necessary to consider AOC values (Fig. 1). The CSF can thus be rewritten as:

$$\text{CSF} = F_{\text{DIC}} + F_{\text{AOC}} + F_{\text{AOC(s)}} = Q \times (n [\text{DIC}] + [\text{AOC}]) / A + F_{\text{AOC(s)}} \quad (7)$$

where  $F_{\text{DIC}}$  and  $F_{\text{AOC}}$  are the DIC and AOC flux via surface runoff, respectively;  $F_{\text{AOC(s)}}$  is the sedimentary flux of AOC in surface water system(s); and  $[\text{DIC}]$  and  $[\text{AOC}]$  are the concentrations of the DIC and AOC at river mouths, respectively (Figs. 1 and 2).

Any prediction of the extent of the carbon sink produced by CCW under global warming and land-use change needs to be corroborated with additional evidence. Satellite observations indicate that the volumes involved in the global hydrologic cycle will increase at a rate of 7% per °C surface warming (Wentz et al., 2007). Raymond et al. (2008), however, argued that land use change and management have been more important than changes in climate and plant  $\text{CO}_2$  fertilization *vis-à-vis* increases in riverine water and carbon export from the Mississippi River over the past 50 years. A vital question is how this applies to other parts of the world.

Finally, it may be noted that DIC concentrations in water in certain settings can be increased by rock weathering due to high concentrations of deep earth  $\text{CO}_2$  (Becker et al., 2008) as well as other inorganic acids such as sulfuric (Lerman et al., 2007; Martin, 2017) and nitric acid (Perrin et al., 2008; Martin, 2017). This increase is not of atmospheric origin, and must be deducted from atmospheric carbon sink calculations. Evaluating the contributions of these mechanisms is a critical component of future research.

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