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Atmospheric CO_2 sink: Silicate weathering or carbonate weathering?

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ABSTRACT

It is widely accepted that chemical weathering of Ca–silicate rocks could potentially control long-term climate change by providing feedback interaction with atmospheric CO_2 drawdown by means of precipitation of carbonate, and that in contrast weathering of carbonate rocks has not an equivalent impact because all of the CO_2 consumed in the weathering process is returned to the atmosphere by the comparatively rapid precipitation of carbonates in the oceans. Here, it is shown that the rapid kinetics of carbonate dissolution and the importance of small amounts of carbonate minerals in controlling the dissolved inorganic C (DIC) of silicate watersheds, coupled with aquatic photosynthetic uptake of the weathering-related DIC and burial of some of the resulting organic C, suggest that the atmospheric CO_2 sink from carbonate weathering may previously have been underestimated by a factor of about 3, amounting to 0.477 Pg C/a. This indicates that the contribution of silicate weathering to the atmospheric CO_2 sink may be only 6%, while the other 94% is by carbonate weathering. Therefore, the atmospheric CO_2 sink by carbonate weathering might be significant in controlling both the short-term and long-term climate changes. This questions the traditional point of view that only chemical weathering of Ca–silicate rocks potentially controls long-term climate change.

1. Introduction

It is widely accepted that chemical weathering of Ca–silicate rocks could potentially control long-term (50–100 Ma episodicity) climate change by providing feedback interaction with atmospheric CO_2 drawdown by means of the precipitation of carbonate (CO_2 + $CaSiO_3 \Rightarrow CaCO_3$ + SiO_2), and that in contrast weathering of carbonate rocks has not an equivalent impact because all CO_2 consumed in dissolution of carbonates is returned to the atmosphere by the comparatively rapid precipitation of carbonates in the oceans ($CaCO_3 + CO_2 + H_2O \Longleftrightarrow Ca^2 + +2HCO_3^-$) (Berner et al., 1983; Elderfield, 2010; Urey, 1952). Thus, the proportions of silicate and carbonate weathering at the earth's surface are important in long-term global CO_2 balances (Berner et al., 1983).

However, for short timescales <3 ka (i.e., the turnover time of the oceans, Oki, 1999), the role of carbonate weathering in the global CO_2 cycle and thus in short-term climate changes cannot be ignored due to the much faster kinetics of dissolution (Dreybrodt, 1988; Kump et al., 2000; Liu and Dreybrodt, 1997; Plummer et al., 1978), and the much greater solubility of carbonates (Dreybrodt, 1988; Holland, 1978; Hurd et al., 1979; Van Cappellen and Qiu, 1997) compared to silicates. Moreover, the presence of the "biological carbon pump" in natural aquatic ecosystems (e.g., oceans, lakes, rivers, reservoirs) diverts C into the lithosphere by sedimentation and burial of organic C produced by the aquatic photosynthetic uptake of weathering-related dissolved inorganic C (DIC) (Einsele et al., 2001; Lerman and Mackenzie, 2005; Maier-Reimer, 1993; McElroy, 1983; Smith, 1981; Smith and Gattuso, in press):

$$Ca^{2+} + 2HCO_3^- \Rightarrow CaCO_3 + \Psi(CO_2 + H_2O) + (1 - \Psi)(CH_2O + O_2). \tag{1}$$

This has been neglected in the long-term timescale-related global C cycle models. For example, Berner et al. (1983) suggests that the organic sequestration is compensated by the oxidation of fossil organic matter and assumes steady state. In the short-term timescale-related global C cycle models, the effect of the "biological carbon pump" in natural aquatic ecosystems is concentrated on the oceans but not on the continents (Lerman and Mackenzie, 2005; Maier-Reimer, 1993; McElroy, 1983; Smith, 1981; Smith and Gattuso, in press). Therefore, the atmospheric CO_2 sink due to carbonate weathering (reaction (1)) may have previously been greatly underestimated.

2. Further exploration of recent key references

Though rich in carbonate rocks, calcite is also commonly associated with shales (Hurd et al., 1979), metamorphosed gneisses and schists, hydrothermal altered granitic rocks (Blum et al., 1998), and pristine granitoids, which probably form from CO_2-rich fluids asso-

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ciated with the final cooling of batholiths as well as during later periods of hydrothermal activity (White et al., 1999). Therefore, the CO_2 consumed in silicate areas does not necessarily result primarily from silicate weathering: it may mainly be due to the contribution of rapid calcite dissolution in the silicate rocks (Blum et al., 1998; White et al., 1999, 2005). For example, Blum et al. (1998) investigated the major element and Sr isotope geochemistry of surface waters, bedrock, and river sands in the Raikhot watershed within the High Himalayan Crystalline Series (HHCS) of northern Pakistan. Mass-balance calculations of mineral-weathering contributions to the dissolved flux of ions from the watershed indicated that 82% of the HCO_3^- flux is derived from weathering of carbonate minerals and only 18% from silicate weathering, even though the bedrock in the watershed is predominantly quartzofeldspathic gneiss and granite with only ~1% carbonate. This study demonstrated the importance of small amounts of bedrock carbonate in controlling the water chemistry of glaciated silicate watersheds. It also suggests that the flux of Sr with a high $^{87}Sr/^{86}Sr$ ratio in the major Himalayan rivers may be derived mainly from weathering of low amounts of calcite within the HHCS silicates. Therefore, models using the flux of radiogenic Sr from the Himalayas as a proxy for silicate weathering rates may overestimate the amount of CO_2 consumption attributable to reactions with silicates there. Similar results were obtained by Jacobson et al. (2002b), who showed that the conventional application of two-component Ca/Sr and $^{87}Sr/^{86}Sr$ mixing equations has overestimated silicate-derived Sr^{2+} and HCO_3^- fluxes from the glaciated Himalaya. They found that carbonate dissolution provides more than 90% of the weathering-derived Ca^{2+}, HCO_3^-, and Sr for at least 55 ka following initial exposure of rock surfaces, although carbonate may represent only ~1.0 wt.% in fresh glacial till (Jacobson et al., 2002a): this significantly increases the Ca^{2+}/Na^+ and HCO_3^-/Na^+ ratios in the so-called 'silicate end member reservoir'. In addition, Jacobson et al. (2002b) found that (1) carbonate bedrock in the Himalaya has a wide range of Ca/Sr and $^{87}Sr/^{86}Sr$ ratios that cannot be adequately defined by a single end member in conventional mass-balance equations, and (2) Ca^{2+} behaves non-conservatively during transport in Himalayan stream waters. The removal of up to 70% of the dissolved Ca^{2+} by calcite precipitation appears to be a pervasive process in the Himalaya that drives dissolved Ca/Sr ratios toward values much lower than those measured in carbonate bedrock. Therefore, they concluded that without taking these factors into account, stream water Ca/Sr and $^{87}Sr/^{86}Sr$ ratios, and hence HCO_3^-, can be erroneously interpreted to represent the dominance of silicate dissolution (Jacobson et al., 2002b). The present authors think similar problems could occur with the inversion method if one uses ratios of Ca/Na and HCO_3/Na. This may explain why Gaillardet et al. (1999) obtained such high CO_2 consumption estimates by silicate weathering despite the fact that the silicate weathering rates are 10^2–10^8 times lower than those of carbonates. They calculated the CO_2 consumption by silicate weathering from the bulk chemistry of large rivers and underestimated the contributions of carbonate weathering that occur in predominantly silicate areas.

To summarize, the contribution of carbonate weathering to the atmospheric CO_2 sink may have been greatly underestimated in these previous studies (Amiotte-Suchet and Probst, 1995; Berner et al., 1983; Gaillardet et al., 1999; Meybeck, 1987).

In a new attempt to estimate the atmospheric CO_2 budget, by considering the combined effects of carbonate dissolution, the global water cycle and photosynthetic uptake of dissolved inorganic C($DIC = CO_2(aq) + HCO_3^- + CO_3^{2-}$) by aquatic organisms (see Fig. 1), Liu et al. (2010) found that the net atmospheric CO_2 sink by carbonate weathering on the continents (including dissolution of CO_2 in non-carbonate areas) could be as large as 0.477 Pg C/a (CFR + CFA in Fig. 1). This is much larger (by a factor of about 3) than the estimate of 0.148 Pg C/a obtained by Gaillardet et al. (1999), who underestimated the carbonate weathering sink in silicate areas and did not consider the photosynthetic uptake of DIC by continental aquatic organisms and burial of some of the resulting organic matter on the continents ($1 - \Psi = 0.8$, So CFA = 0.233 Pg C/a, see Fig. 1). This value of 0.233 Pg C/a has been confirmed by the independent work of Dean and Gorham (1998), Einsele et al. (2001), and Cole et al. (2007). They estimated that about 0.2–0.3 Pg C/a, mainly of autochthonous origin (i.e., mainly by the reaction (1)), is buried in aquatic sediments in inland waters (lakes, reservoirs and rivers). Therefore, the atmospheric CO_2 sink due to carbonate weathering reaction (1) has previously been greatly underestimated. If the value by Jacobson et al. (2002a) (i.e. about 10% of HCO_3^- originates from silicate weathering) is applied to the case of Gaillardet et al. (1999), then the atmospheric CO_2 sink by silicate weathering will decrease from 0.14 Pg C/a (Gaillardet et al., 1999) to about 0.014 Pg C/a, and correspondingly, the atmospheric CO_2 sink by carbonate weathering will increase from 0.148 Pg C/a (Gaillardet et al., 1999) to 0.211 Pg C/a ($0.148 + (0.14–0.014) * 0.5 = 0.211$, where the factor 0.5 results from the fact that in the case of carbonate dissolution only half of the HCO_3^- is of atmospheric origin). Therefore, the atmospheric CO_2 sink by carbonate weathering is 15-times that of the atmospheric CO_2 sink by silicate weathering. In other words, the atmospheric CO_2 sink by carbonate weathering contributes about 94% to the atmospheric CO_2 sink, while only 6% results from silicate weathering.

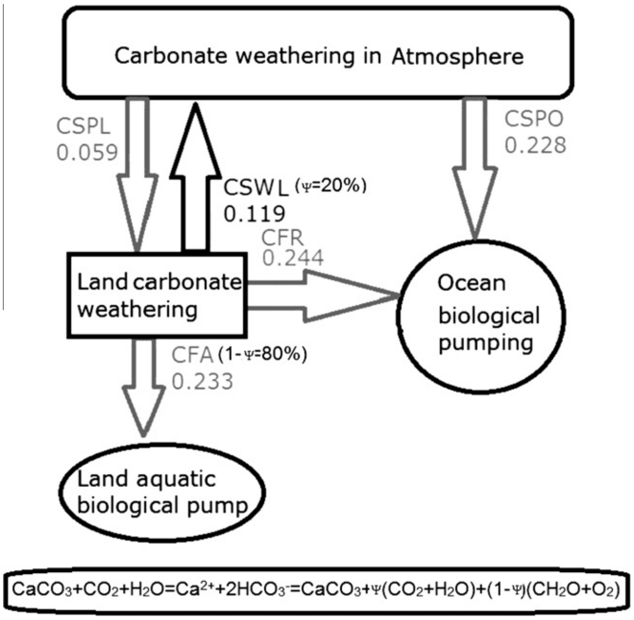

Fig. 1. Atmospheric CO_2 sinks (in Pg C/a) by carbonate weathering (i.e., carbonate dissolution, coupled with aquatic photosynthetic uptake of the resulting dissolved inorganic carbon). CSPL: carbon sink by precipitation on land; CSPO: carbon sink by precipitation in oceans; CSWL: carbon source from waters on land; CFR: carbon flux to oceans by rivers; CFA: carbon flux by aquatic plants to organic matter burial sites (modified after Liu et al. (2010)).

3. Conclusions

It has been shown that the rapid kinetics of carbonate dissolution and the importance of small amounts of carbonate minerals in controlling dissolved inorganic C (DIC) of silicate watersheds, coupled with aquatic photosynthetic uptake of the weathering-related DIC and burial of some of the resulting organic C, suggest that the atmospheric CO_2 sink by carbonate weathering may previously have been underestimated by a factor of about 3, amounting to 0.477 Pg C/a. This indicates that the contribution of silicate weathering to atmospheric CO_2 sink may be only 6%, while the other 94% is by carbonate weathering.

The new findings on the magnitude of the carbonate weathering-related atmospheric CO_2 sink (Liu et al., 2010) are significant in 3 respects.

First, the origin of carbonates in oceans and lakes must be questioned since the occurrence of aquatic photosynthetic organisms. Is it mainly due to the silicate weathering reaction?

$$CaSiO_3 + CO_2 \Rightarrow CaCO_3 + SiO_2 \tag{2}$$

or is it mainly due to the carbonate weathering reaction (Lerman and Mackenzie, 2005; Smith and Gattuso, in press)?

$$\begin{aligned} CaCO_3 + CO_2 + H_2O &\Rightarrow Ca^{2+} + 2HCO_3^- \\ &\Rightarrow CaCO_3 + \Psi(CO_2 + H_2O) + (1 - \Psi) \\ &\quad \times (CH_2O + O_2)? \end{aligned} \tag{3}$$

Because of the much faster kinetics of carbonate weathering, the carbonates in oceans and lakes may originate mainly from (3), the carbonate reaction.

Second, the atmospheric CO_2 sink by rock weathering since the occurrence of aquatic photosynthetic organisms must be reassessed. It appears that the atmospheric CO_2 sink in chemical weathering rests chiefly in carbonate dissolution and subsequent aquatic photosynthetic uptake of the resulting DIC (Liu et al., 2010). However, for accurate quantification, the consumption of CO_2 by silicate and carbonate weathering, the balance between the production/burial and respiration/oxidation of organic matter, and the fluxes of CO_2 release from the continental aquatic ecosystems must together all be taken into account in future studies.

Third, the presence of a “biological carbon pump effect” in natural aquatic ecosystems which diverts C produced by the reaction $Ca^{2+} + 2HCO_3^- \Rightarrow CaCO_3 + \Psi(CO_2 + H_2O) + (1 - \Psi)(CH_2O + O_2)$ to the lithosphere by sedimentation and burial of the organic C (Lerman and Mackenzie, 2005; Smith and Gattuso, in press), implies that the atmospheric CO_2 sink in carbonate weathering might also be significant in controlling long-term climate change. This questions the traditional point of view (Berner et al., 1983) that only chemical weathering of Ca–silicate rocks could potentially control long-term climate change by providing feedback interactions with atmospheric CO_2 drawdown due to the precipitation of carbonate.

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