Earth and Planetary Science Letters 485 (2018) 111–120

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Relationships between CO_2, thermodynamic limits on silicate weathering, and the strength of the silicate weathering feedback

Matthew J. Winnick*, Kate Maher

Department of Geological Sciences, Stanford University, Stanford, CA, USA

A R T I C L E I N F O

Article history:
Received 31 July 2017
Received in revised form 5 January 2018
Accepted 6 January 2018
Editor: D. Vance

Keywords:
chemical weathering
negative feedback
thermodynamic limits
carbon cycle
geobiology
paleoclimate

A B S T R A C T

Recent studies have suggested that thermodynamic limitations on chemical weathering rates exert a first-order control on riverine solute fluxes and by extension, global chemical weathering rates. As such, these limitations may play a prominent role in the regulation of carbon dioxide levels (pCO_2) over geologic timescales by constraining the maximum global weathering flux. In this study, we develop a theoretical scaling relationship between equilibrium solute concentrations and pCO_2 based on equilibrium constants and reaction stoichiometry relating primary mineral dissolution and secondary mineral precipitation. We test this theoretical scaling relationship against reactive transport simulations of chemical weathering profiles under open- and closed-system conditions, representing partially and fully water-saturated regolith, respectively. Under open-system conditions, equilibrium bicarbonate concentrations vary as a power-law function of pCO_2 ($y = kx^n$) where n is dependent on reaction stoichiometry and k is dependent on both reaction stoichiometry and the equilibrium constant. Under closed-system conditions, bicarbonate concentrations vary linearly with pCO_2 at low values and approach open-system scaling at high pCO_2. To describe the potential role of thermodynamic limitations in the global silicate weathering feedback, we develop a new mathematical framework to assess weathering feedback strength in terms of both (1) steady-state atmospheric pCO_2 concentrations, and (2) susceptibility to secular changes in degassing rates and transient carbon cycle perturbations, which we term 1st and 2nd order feedback strength, respectively. Finally, we discuss the implications of these results for the effects of vascular land plant evolution on feedback strength, the potential role of vegetation in controlling modern solute fluxes, and the application of these frameworks to a more complete functional description of the silicate weathering feedback. Most notably, the dependence of equilibrium solute concentrations on pCO_2 may represent a direct weathering feedback largely independent of climate and modulated by belowground organic carbon respiration.

1. Introduction

The stability of global temperatures within the range of planetary habitability over 4 billion years requires a tightly coupled negative feedback system within the carbon cycle to regulate atmospheric greenhouse gas concentrations (Urey, 1952). This feedback system is thought to be the drawdown of atmospheric CO_2 by terrestrial silicate weathering coupled with oceanic carbonate deposition (Walker et al., 1981), potentially modulated by the net oxidation and burial of organic carbon (Petsch et al., 2000; France-Lanord and Derry, 1997) and sulfide minerals (Torres et al., 2014). In this framework, weathering rates dynamically balance tectonic degassing rates and net organic carbon burial and oxidation, as well as transient carbon cycle perturbations. During transient (<1 Ma) carbon cycle perturbations, silicate weathering also sets the recovery timescale of the ocean–atmosphere system through the rate at which excess CO_2 is sequestered or deficit CO_2 is replenished (Sundquist, 1991; Archer, 2005). Although many previous studies have characterized the mathematical form of the silicate weathering feedback as a function of CO_2, these have historically focused on the dependence of mineral dissolution kinetics on CO_2 concentrations and temperatures (*e.g.* Walker et al., 1981; Berner et al., 1983; Velbel, 1993; Kump et al., 2000; West, 2012). In contrast, recent work has suggested that thermodynamic limitations to weathering act as a first-order component of the silicate weathering feedback (Maher and Chamberlain, 2014) and may in turn vary as a function of CO_2 in the weathering environment (Calmels et al., 2014).

---

* Corresponding author at: 450 Serra Mall Bldg. 320, Stanford, CA, 94305, USA.
E-mail address: mwinnick@stanford.edu (M.J. Winnick).

https://doi.org/10.1016/j.epsl.2018.01.005
0012-821X/© 2018 Elsevier B.V. All rights reserved.

Thermodynamic limitations to weathering describe the approach to a metastable equilibrium involving dissolving minerals and precipitating secondary phases. When residence times of subsurface waters are greater than the time needed to reach this metastable equilibrium, solute concentrations remain constant over a wide range of discharge values. Under these conditions, solute fluxes become linearly dependent on discharge (Maher, 2011) resulting in 'chemostatic' behavior. In terms of the silicate weathering feedback, the thermodynamic limit can be thought of as the maximum potential weathering rate for given environmental (*i.e.* temperature, runoff, vegetation) and lithological boundary conditions. Additionally, the widespread observation of near-chemostatic behavior across small (Godsey et al., 2009; HCO_3^- *log–log* slopes of -0.05 to -0.15) and major river systems (Moon et al., 2014; median HCO_3^- *log–log* slope of -0.16) suggest that thermodynamic limitations may play an important role in controlling riverine solute fluxes. Here, we explore the relationships between CO_2 in the weathering zone, thermodynamic limits on solute concentrations, and the role of such limits in governing the strength of the silicate weathering negative feedback.

The concept of silicate weathering feedback strength has been present in the literature since the 1980s and has been used to describe multiple phenomena. These include both (1) the role of weathering in setting steady-state atmospheric $p\mathrm{CO}_2$ for a given volcanic degassing rate; and (2) the response of atmospheric $p\mathrm{CO}_2$ to perturbations in the carbon cycle, such as secular changes in degassing rates and transient carbon release events. The first of these effects arises from the fact that, due to the relatively small reservoir size of the atmosphere–ocean system ($\sim 3 \times 10^{18}$ mol C) compared to the magnitude of the input and removal fluxes of carbon ($\sim 8 \times 10^{18}$ mol C My^{-1}) (Gaillardet et al., 1999), weathering fluxes must balance tectonic degassing and organic carbon burial/oxidation on timescales of $>10^5$ yrs in order to maintain habitable conditions (Berner and Caldeira, 1997; Caves et al., 2016). Accordingly, steady-state atmospheric $p\mathrm{CO}_2$ is determined by the value at which weathering fluxes equal degassing fluxes. The second effect refers to the sensitivity of weathering fluxes to changes in atmospheric $p\mathrm{CO}_2$ and controls both the response of steady-state $p\mathrm{CO}_2$ to a change in secular degassing rates and the recovery timescale in response to transient carbon release events (Sundquist 1991; Archer, 2005; Uchickawa and Zeebe, 2008). Despite these effects being described throughout the literature, there has as yet been no formal classification for these effects as separate, though related, phenomena.

Herein, we present mathematical frameworks for quantifying the dependence of equilibrium solute concentrations on $p\mathrm{CO}_2$ and for assessing the strength of the silicate weathering feedback in terms of driving both steady-state atmospheric $p\mathrm{CO}_2$ and the sensitivity of atmospheric $p\mathrm{CO}_2$ to carbon cycle perturbations. Theoretical arguments are supported by reactive transport simulations of weathering profiles. Finally, we discuss the implications of these theoretical arguments for the silicate weathering effects caused by the rise and spread of vascular land plants, the role of plant productivity in controlling modern weathering fluxes, and the potential role of thermodynamic limits as a direct feedback between weathering rates and atmospheric CO_2 concentrations independent of climate.

2. Mathematical framework

2.1. First v. second order silicate weathering feedback strength

In order to examine the effects of thermodynamic limitations on the global silicate weathering feedback, we first develop a mathematical framework to assess feedback strength. Although the silicate weathering negative feedback system has been described extensively in the literature, descriptions of feedback strength have historically referred to two separate phenomena. Specifically, the strength of the negative feedback has been used to describe both (1) steady-state atmospheric $p\mathrm{CO}_2$ given tectonic degassing and organic burial/oxidation rates (*e.g.* Berner et al., 1983; Caves et al., 2016); and (2) the response of atmospheric $p\mathrm{CO}_2$ to perturbations in degassing and organic carbon burial/oxidation rates (*e.g.* Sundquist, 1991; Archer, 2005; Uchikawa and Zeebe, 2008).

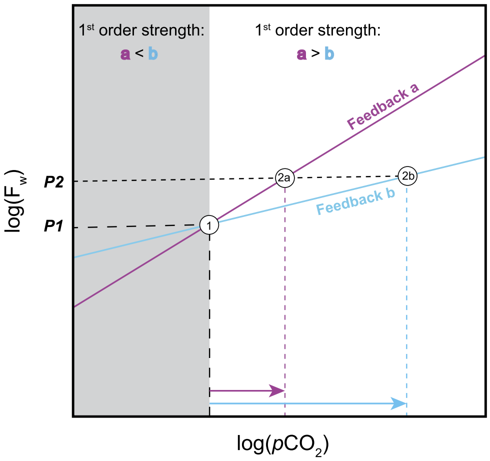

Fig. 1. Conceptual diagram of 1st and 2nd order silicate weathering feedback strengths for two functional forms of the feedback, Feedbacks a and b. Gray and white shaded areas indicate relative 1st order feedback strength. Colored arrows denote the response of $p\mathrm{CO}_2$ to long-term changes in degassing rates from P1 to P2.

As demonstrated in previous studies, steady-state atmospheric $p\mathrm{CO}_2$ is set by the functional dependence of chemical weathering rates on atmospheric $p\mathrm{CO}_2$ as conceptualized in Fig. 1. At any given CO_2 production rate (P) representing CO_2 degassing, atmospheric $p\mathrm{CO}_2$ is set by the $p\mathrm{CO}_2$ value at which the silicate weathering flux (F_w) is equal to P (Berner et al., 1983; Caves et al., 2016). The weathering feedback is commonly represented in global carbon-cycle models as a power-law equation, approximating empirical dependencies of weathering rates on climatic variables (e.g. Walker et al., 1981; Berner, 1991; Uchikawa and Zeebe, 2008). Given the power-law functional form of the silicate weathering feedback,

$$F_w = k \cdot (p\mathrm{CO}_2)^n, \tag{1}$$

steady-state atmospheric $p\mathrm{CO}_2$ varies as a function of k and n, which together represent global weatherability (Kump and Arthur, 1997; Kump et al., 2000). When the Earth system has a higher weatherability, for example due to more reactive surface lithology, steady-state atmospheric $p\mathrm{CO}_2$ for a given degassing rate is lower and the strength of the weathering feedback is said to be higher. We define this aspect, based on the absolute value of weathering rates at a given $p\mathrm{CO}_2$, as the 1st order feedback strength. This definition of feedback strength incorporates both k and n values as they combine to set the silicate weathering flux for a given $p\mathrm{CO}_2$.

In Fig. 1, we demonstrate differences in 1st order feedback strength between two power-law feedback functions, as represented by the value of F_w at any given $p\mathrm{CO}_2$. At Point 1 where these weathering curves intersect, $F_w(p\mathrm{CO}_2)$ is the same, indicating the same 1st order feedback strength. At lower $p\mathrm{CO}_2$, Feedback b has a higher 1st order feedback strength (gray shading), and at higher $p\mathrm{CO}_2$, Feedback a has a higher 1st order feedback strength.

The second feedback phenomenon refers to how susceptible the climate is to carbon cycle perturbations. This aspect of feedback strength is controlled by the slope of the weathering curve, which represents the sensitivity of weathering rates to changes in $p\mathrm{CO}_2$.