

The impact of denitrification on the atmospheric CO₂ uptake potential of seawater

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ABSTRACT

In addition to carbonate dissolution, denitrification represents another pivotal geochemical process that produces alkalinity in the marine environment. Previous studies suggested that such alkalinity can increase seawater buffering capacity and thus enhance atmospheric CO₂ uptake when the denitrifying water is exposed to the air in the coastal ocean. In this study, we explored the potential responses of seawater pCO₂ to denitrification through three approaches: (1) simulating pCO₂ variations in response to various denitrification scenarios, (2) verifying *in situ* pCO₂ data in a well-known denitrification “hotbed”—the Arabian Sea—as well as in anammox-dominated oxygen minimum waters in the Eastern South Pacific, and (3) examining published benthic alkalinity and dissolved inorganic carbon (DIC) flux ratios. In the first approach, we showed that the ratios of alkalinity and DIC addition during denitrification of different model compounds were lower than the slopes of alkalinity and DIC ($\Delta TA/\Delta DIC$) along a series of CO₂ isopleths corresponding to modern-day xCO₂ at different temperatures. In the second approach, we showed that water pCO₂ level increased with loss of fixed nitrogen. Last, we showed that benthic alkalinity and DIC flux ratios were also lower than the $\Delta TA/\Delta DIC$ values derived from the above mentioned CO₂ isopleths. Overall, these independent approaches support the conclusion that denitrification-generated alkalinity (together with other alkalinity-altering anaerobic respiration pathways) may not be a notable driving force for enhancing atmospheric CO₂ uptake, and concurrent DIC production during denitrification has to be taken into account when discussing changes in seawater buffering capacity along with alkalinity production.

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1. Introduction

Since the Industrial Revolution, about 40% of the anthropogenic CO₂ emitted to the atmosphere has been absorbed by the ocean (Sabine et al., 2004). However, recent findings suggest that the ocean's capacity for further CO₂ uptake may be weakening (Doney et al., 2009; Sabine and Tanhua, 2010). Therefore, understanding biogeochemical processes that may enhance or decrease this capacity becomes increasingly important. CO₂ uptake by seawater depends on the seawater buffering capacity, or the Revelle factor (Revelle and Suess, 1957), which is linked to the ratio of dissolved inorganic carbon (DIC) and alkalinity in seawater (Broecker and Peng, 1982). The balance between DIC and alkalinity determines CO₂ partial pressure (pCO₂) of a seawater parcel (Eggleston et al., 2010; Frankignoulle, 1994; Millero, 2001), and the pCO₂ gradient between the surface seawater and the atmosphere exerts thermodynamic control over the direction of CO₂ flux.

It has been suggested that alkalinity production caused by the dissolution of sedimentary carbonate, mostly in tropical shallow-water areas, could alleviate the atmospheric CO₂ problem (Burdige and

Zimmerman, 2002; Sabine and Mackenzie, 1995). This reaction occurs through



In addition to carbonate dissolution, alkalinity produced via metabolic processes that do not require oxygen (for example, denitrification, sulfate reduction, and metal reduction), has also been recognized in the literature (Chen, 2002; Thomas et al., 2009; Van Cappellen and Wang, 1996), although estimates of the magnitude of this alkalinity production were mostly based on incomplete redox cycles of nitrogen and sulfur (see discussion in Hu and Cai, 2011, for a review). This type of alkalinity production (in particular denitrification) has been proposed to enhance oceanic CO₂ storage, since CO₂ released in these reactions is present in the form of alkalinity, not CO₂ (Thomas et al., 2009). However, alkalinity-associated CO₂ storage may be valid only on regional scales if the system examined receives nitrate from external sources, and its global significance is likely small (Hu and Cai, 2011). Moreover, some studies also have suggested that anaerobic alkalinity production (in particular that from denitrification) may increase the seawater buffering capacity of the coastal ocean, enhancing atmospheric CO₂ sequestration (Fennel, 2010; Fennel et al., 2008; Thomas et al., 2009).

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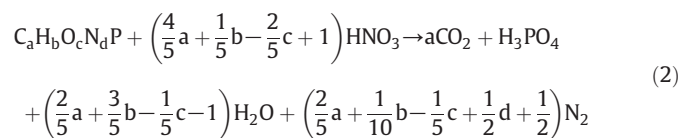
In this work, we attempted to elucidate how denitrification affects seawater $p\text{CO}_2$ using three approaches: (1) we used numerical simulation to predict the direction of $p\text{CO}_2$ change in response to various denitrification scenarios; (2) we calculated *in situ* $p\text{CO}_2$ data in a well-known denitrification “hotbed”—the Arabian Sea, and in an anammox-dominated oxygen minimum zone in the Eastern South Pacific, to examine the relationship between seawater $p\text{CO}_2$ and net water column nitrate loss; and (3) we examined the published benthic alkalinity and DIC flux ratios and used these ratios to predict seawater $p\text{CO}_2$ change in response to benthic fluxes. Based on these approaches, we found that alkalinity generated through denitrification (even when combined with other anaerobic respiration pathways) is unlikely a driving force for depressing seawater $p\text{CO}_2$. Thus the resulting seawater cannot be a sink for atmospheric CO_2 simply due to the occurrence of denitrification.

2. Theoretical considerations

Denitrification reactions using marine organic matter (OM) as the substrate have different reaction stoichiometries that depend on the elemental composition of the remineralizing OM (Koeve and Kähler, 2010). Our understanding of marine OM composition has come a long way, from the classical finding of the “Redfield ratio”—i.e., $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ based on direct analysis of fresh phytoplankton (Redfield, 1934, 1958), to more recent studies based on water mass carbon and nutrient regeneration studies (Anderson and Sarmiento, 1994; Boulahdid and Minster, 1989; Li et al., 2000; Li and Peng, 2002; Minster and Boulahdid, 1987; Pahlow and Riebesell, 2000). Further studies using ocean circulation modeling approaches (Mills and Arrigo, 2010; Weber and Deutsch, 2010) and direct analyses of phytoplankton species growing in different nutrient conditions reveal even more diverse elemental compositions (Geider and La Roche, 2002; Quigg et al., 2003). Although the elemental ratios of previously studied marine OM occur over a wide range, from the perspective of organic matter remineralization stoichiometry, those water column studies that directly involved examination of the proportional release of nutrients and inorganic carbon should be more relevant to our discussion because changes in the inorganic carbon system dominate $p\text{CO}_2$ changes in seawater. In addition, to simplify this discussion, we assume that both aerobic respiration and denitrification release the nutrient elements (N, P, and Si) and DIC in the same proportions (Gruber and Sarmiento, 1997; Paulmier et al., 2009).

A generalized formula for remineralizing OM can be written as $\text{C}_a\text{H}_b\text{O}_c\text{N}_d\text{P}$. Here subscripts a, b, c, and d all have a range of values

(Paulmier et al., 2009). A complete denitrification reaction in which all fixed nitrogen is eventually converted to N_2 gas can be written in the following fashion (Paulmier et al., 2009):



In this reaction, alkalinity increase caused by denitrification is $4/5a + 1/5b - 2/5c$ per unit of OM remineralization, which equals the difference between the consumption of nitric acid and production of one unit of phosphoric acid. From Rxn. (2), it is clear that alkalinity production is $(4/5a + 1/5b - 2/5c)/a$ for every unit of DIC production. We defined this TA and DIC production ratio (i.e., $(4/5a + 1/5b - 2/5c)/a$) as R ($\delta\text{TA}/\delta\text{DIC}$). Therefore, remineralization of OM of different elemental compositions (specifically the C/H ratio, e.g., Anderson, 1995) requires different amounts of electron acceptors: thus denitrification reactions using these different forms of OM yield different R values. Note that aerobic respiration always yields slightly negative alkalinity, hence negative R , due to the production of nitric and phosphoric acids. Table 1 summarizes the results from water column nutrient studies on the remineralization of OM of different compositions, and we refer to these formulas as representing different model compounds.

For a parcel of seawater that is in contact with the atmosphere, according to Fick's first law, the thermodynamic controlling factor on the direction of CO_2 flux (i.e., in or out of seawater) depends on the chemical gradient of $p\text{CO}_2$ between seawater and the atmosphere. For simplicity of the following discussion, we assumed that our starting water parcel is in equilibrium with atmospheric CO_2 . Then, if aerobic respiration occurs, a net increase in DIC and slight decrease in alkalinity (see above) will always increase seawater $p\text{CO}_2$, and as a result, this water parcel will act as a CO_2 source to the atmosphere. On the other hand, to determine whether a water parcel that is undergoing denitrification can take up atmospheric CO_2 after being exposed to the air (Fennel, 2010; Thomas et al., 2009), we needed to examine whether the addition of alkalinity and DIC (i.e., δTA and δDIC) into this water parcel via denitrification decreases the water $p\text{CO}_2$ level. Furthermore, to consider the effect of denitrification on seawater $p\text{CO}_2$, two different scenarios of denitrification in the marine environment have to be examined. One is the canonical (classical) denitrification, which uses nitrate from external sources (Rxn. 2). The other is the so-called “coupled

Table 1

Elemental composition of remineralizing organic matter based on water column studies and corresponding O_2 demand per unit of phosphorous release, apparent oxidation state (AOS) of organic carbon, and $\delta\text{TA}/\delta\text{DIC}$ ratio (R) during a canonical denitrification reaction.

No	OM formula (C:H:O:N:P elemental composition) ^f	O_2 Demand ^a	AOS ^b	R	Reference
1	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ ($\text{C}_{106}\text{H}_{163}\text{O}_{110}\text{N}_{16}\text{P}$)	138	0.0	0.88	Redfield (1934)
2	$\text{C}_{25}(\text{CH}_2\text{O})_{101}(\text{CH}_4)_9(\text{NH}_3)_{13}(\text{H}_3\text{PO}_4)$ ($\text{C}_{135}\text{H}_{280}\text{O}_{105}\text{N}_{13}\text{P}$)	170	-0.3	0.90	Li et al. (2000)
3	$\text{C}_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)\text{H}_{48}(\text{H}_2\text{O})_{38}$ ($\text{C}_{106}\text{H}_{175}\text{O}_{42}\text{N}_{16}\text{P}$) ^c	150	-0.5	0.97	Anderson (1995)
4	$\text{C}_{122}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)\text{H}_{72}(\text{H}_2\text{O})_n$ ($\text{C}_{122}\text{H}_{123}\text{O}_4\text{N}_{16}\text{P}$) ^d	172	-0.6	0.99	Takahashi et al. (1985)
5	$\text{C}_{117}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)\text{H}_{84}(\text{H}_2\text{O})_n$ ($\text{C}_{117}\text{H}_{135}\text{O}_4\text{N}_{16}\text{P}$) ^d	170	-0.7	1.02	Anderson and Sarmiento (1994)
6	$\text{C}_{80}(\text{NH}_3)_{15}(\text{H}_3\text{PO}_4)\text{H}_{92}(\text{H}_2\text{O})_n$ ($\text{C}_{80}\text{H}_{140}\text{O}_4\text{N}_{15}\text{P}$) ^e	133	-1.2	1.13	Li and Peng (2002)
7	$\text{C}_{73}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)\text{H}_{128}(\text{H}_2\text{O})_n$ ($\text{C}_{73}\text{H}_{179}\text{O}_4\text{N}_{16}\text{P}$) ^e	137	-1.8	1.27	Li and Peng (2002)

^a O_2 demands were calculated assuming all fixed nitrogen is eventually oxidized to nitrate. The result is per unit of phosphoric acid release (i.e., per unit of organic matter remineralization) (Paulmier et al., 2009).

^b Organic carbon oxidation states were calculated using different OM formulas by assuming the oxidation states of hydrogen, organic nitrogen, and phosphorous as +1, -3, and +5, respectively.

^c OM formula was predicted using the bulk elemental composition given in Anderson (1995).

^d Both the OM formula and elemental ratio were calculated using the reaction stoichiometry in respective references.

^e Both the OM formula and elemental ratio were calculated using the reaction stoichiometry in respective references, and the values were from the South Atlantic Ocean and North Atlantic Ocean, respectively.

^f Using reaction stoichiometry only, the specific “water” (as H_2O) content in the organic molecules could not be estimated. In the elemental composition (parentheses), we elected to omit the proportion of hydrogen and oxygen that can be considered as H_2O (which does not lead to oxygen consumption or TA/DIC production, see Anderson, 1995) and only counted the four oxygen atoms in the phosphate group.

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