

An assessment of ocean margin anaerobic processes on oceanic alkalinity budget

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[1] Recent interest in the ocean's capacity to absorb atmospheric CO₂ and buffer the accompanying "ocean acidification" has prompted discussions on the magnitude of ocean margin alkalinity production via anaerobic processes. However, available estimates are largely based on gross reaction rates or misconceptions regarding reaction stoichiometry. In this paper, we argue that net alkalinity gain does not result from the internal cycling of nitrogen and sulfur species or from the reduction of metal oxides. Instead, only the processes that involve permanent loss of anaerobic remineralization products, i.e., nitrogen gas from net denitrification and reduced sulfur (i.e., pyrite burial) from net sulfate reduction, could contribute to this anaerobic alkalinity production. Our revised estimate of net alkalinity production from anaerobic processes is on the order of 4–5 Tmol yr⁻¹ in global ocean margins that include both continental shelves and oxygen minimum zones, significantly smaller than the previously estimated rate of 16–31 Tmol yr⁻¹. In addition, pyrite burial in coastal habitats (salt marshes, mangroves, and seagrass meadows) may contribute another 0.1–1.1 Tmol yr⁻¹, although their long-term effect is not yet clear under current changing climate conditions and rising sea levels. Finally, we propose that these alkalinity production reactions can be viewed as "charge transfer" processes, in which negative charges of nitrate and sulfate ions are converted to those of bicarbonate along with a net loss of these oxidative anions.

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1. Introduction

[2] Alkalinity mass balance can be translated into carbonate mass balance because carbonate dissolution and precipitation are the dominant processes that control oceanic alkalinity inventory [e.g., *Berelson et al.*, 2007; *Chung et al.*, 2003]. Thus, the global ocean alkalinity cycle is an important subject in studying both the oceanic carbonate mass balance [*Broecker and Peng*, 1982; *Milliman and Droxler*, 1996; *Morse and Mackenzie*, 1990] and the buffering capacity of seawater in the event of increasing atmospheric CO₂ [e.g., *Feely et al.*, 2004; *Frankignoulle*, 1994]. However, despite many years of study, whether the global carbonate cycle is at steady state and the causes of apparent nonsteady state still remain contentious questions [*Berelson et al.*, 2007; *Iglesias-Rodriguez et al.*, 2002; *Milliman*, 1993; *Milliman and Droxler*, 1996].

[3] The study by *Berner et al.* [1970] was one of the first to examine the issue of elevated carbonate alkalinity in anoxic sediment pore waters, where most of the alkalinity was produced through sulfate reduction. This type of alkalinity production does not involve carbonate dissolution as

has been observed in both shallow and deep sea calcareous sediments [*Archer et al.*, 1989; *Berelson et al.*, 1996; *Jahnke et al.*, 1994, 1997; *Martin and Sayles*, 1996; *Morse et al.*, 1985; *Walter and Burton*, 1990]. A series of studies on the anaerobic alkalinity production was conducted in the early 1990s in Tomales Bay, a narrow estuary of the California coast [*Chambers et al.*, 1994; *Dollar et al.*, 1991; *Smith and Hollibaugh*, 1993]. In this area, net sulfate reduction or burial of reduced sulfur compounds (mostly pyrite) was found to account for almost all of the total alkalinity export. Similarly, nonconservative mixing lines of alkalinity versus salinity in the Satilla and Altamaha river estuaries and adjacent continental shelf of the Georgia coast were observed [*Cai and Wang*, 1998; *Wang and Cai*, 2004]. This observation was also attributed to anaerobic alkalinity production in nearshore marsh sediments [*Cai et al.*, 2010].

[4] Alkalinity production through anaerobic processes in global ocean margins, although recognized in the literature [*Chen*, 2002; *Christensen*, 1989; *Dollar et al.*, 1991; *Thomas et al.*, 2009], has not yet been clearly defined and accounted for in oceanic alkalinity cycle studies. Both *Chen* [2002] and *Thomas et al.* [2009] suggested that this alkalinity is produced at a rate of 16–31 Tmol yr⁻¹. *Chen* [2002] further suggested that anaerobic alkalinity production may contribute to upper ocean excess alkalinity, which was previously interpreted as being caused by biology-mediated carbonate dissolution [*Milliman et al.*, 1999]. However,

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Berelson *et al.* [2007] recently argued that upper ocean alkalinity is likely only controlled by carbonate dissolution/precipitation and export from ocean margins may not be significant.

[5] As our discussion will show later, it is problematic to simply rely on apparent reaction stoichiometry to estimate anaerobic alkalinity production without considering spatial and temporal coupling of the redox cycles of the oxidative species. Instead, we must take a global view from the perspective of the entire oceanic system in examining the magnitude of this alkalinity production.

[6] In this paper, first we discuss the processes that are responsible for alkalinity changes (section 2). Next, we clarify the role of denitrification on alkalinity production by separating nitrate sources (i.e., coupled nitrification/denitrification versus net nitrate input into the oceanic environment). Moreover, we also examine the role of anammox process on alkalinity in comparison with denitrification from a geochemical mass balance point of view (section 3). Then, we estimate the magnitude of pyrite burial in continental shelf sediments, using the previously observed ratio between sedimentary organic carbon and pyrite sulfur (i.e., C/S ratio) [Berner, 1982, 1984; Volkov and Rozanov, 1983] and organic carbon preservation rate (section 4). Note here we define our study domain (i.e., ocean margins) as continental shelves within 200 m water depth, which include river deltas, estuaries, and shelves; however, in denitrification estimations, oxygen minimum zones (OMZs) are also considered. In addition, we also try to incorporate recently published organic carbon preservation in coastal vegetated habitats (i.e., salt marshes, mangroves, and seagrass meadows) and their associated pyrite burial into the overall alkalinity budgetary estimation [Duarte *et al.*, 2005] (section 5). Therefore, based on the above major alkalinity contributing processes, we present an updated value of net anaerobic alkalinity production from within our studied domain to the entire oceanic environment. Finally, we propose a “charge transfer” view that may provide a new perspective for understanding the anaerobic alkalinity production issue (section 6).

2. Processes Governing Alkalinity Changes

[7] The classical definition given by Dickson [1981, 1992] presents alkalinity as a difference between proton acceptors and proton donors at zero level of protons (pK = 4.5):

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [Si(OH)_4^-] + [HS^-] + [NH_3] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \quad (1)$$

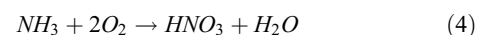
Recently, in their review of biogeochemical reactions that alter seawater alkalinity, Wolf-Gladrow *et al.* [2007] expanded equation (1) by adding a charge balance equation of relevant species to it:

$$TA = [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+] + 2[Sr^{2+}] - [Cl^-] - [Br^-] - [NO_3^-] - TPO_4 + TNH_3 - 2TSO_4 - THF - THNO_2 \quad (2)$$

in which TPO₄, TNH₃, TSO₄, THF, and THNO₂ represent total phosphate, ammonium, sulfate, fluoride, and nitrite species that are present in seawater, respectively (also see an earlier version of equation (2) in the work of Broecker and Peng [1982, p. 67]). Based on equation (2), consumption of cations, such as carbonate precipitation (consuming Ca²⁺ and Mg²⁺) and reverse weathering (consuming Na⁺ and K⁺), would decrease alkalinity. However, these two processes are not relevant to anaerobic remineralization and the magnitude of the latter process remains unclear. Therefore they are not further discussed here. On the other hand, major anion ([Cl⁻], [Br⁻]) and THF concentrations are functions of salinity, and thus are conservative. Furthermore, phosphate concentrations are usually small despite the fact that they can be produced or consumed in early diagenetic reactions [Diaz *et al.*, 2008; Wallmann, 2003], hence its effect on the overall alkalinity budget is also expected to be small. From equations (1)–(2), the changes in the oxidation states of nitrogen and sulfur during biogeochemical processes involve proton production and consumption, thus they contribute to total alkalinity changes. However, apparently neither equation is particularly adequate for interpreting alkalinity changes in reactions that involve reduction of iron and manganese oxides, as Chen [2002] suggested.

[8] In reactions associated with nitrogen species that cause alkalinity changes, photosynthesis produces alkalinity by consuming nitrate (R1 in Table 1 [see also Wolf-Gladrow *et al.*, 2007]). On the other hand, aerobic remineralization returns proton to seawater and thus cancels the alkalinity changes caused by primary production if the CNP ratios of these processes keep the same. A special case in photosynthesis is N₂ fixation, which is expected to cause little net change in alkalinity [Wolf-Gladrow *et al.*, 2007]. However, subsequent aerobic remineralization of organic matter produced by N₂ fixation generates acid (HNO₃). Thus coupled nitrogen fixation and aerobic remineralization causes a net alkalinity drawdown by producing excess acid [Wolf-Gladrow *et al.*, 2007].

[9] In discussing the role of the nitrogen cycle on alkalinity production problems, it is worth noting that ammonia does not lead to system-wide alkalinity change because ammonia is produced through incomplete oxidation of organic matter and is an intermediate product, thus this notion is different from the operational definition that ammonia is counted toward titration alkalinity in seawater samples (equations (1) and (2)). The net effect of ammonification (Reaction (3)) and nitrification (Reaction (4)) produces nitric acid, which is subsequently consumed during the denitrification process (R2 in Table 1). Thus a complete coupling of these processes does not lead to net alkalinity gain.



[10] Coupled nitrification/denitrification widely occurs in continental shelf sediments [Seitzinger *et al.*, 2006]. Since bottom waters in most continental shelves are well-oxygenated, dissolved oxygen facilitates nitrification of

Table 1. Organic Matter Production and Major Remineralization Reactions^a

Reaction Number	Reaction ^b
R1	$106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{OM} + 138\text{O}_2$
R2	$\text{OM} + 84.8\text{HNO}_3 \rightarrow 106\text{CO}_2 + 42.4\text{N}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
R3	$\text{OM} + 212\text{MnO}_2 + 424\text{H}^+ \rightarrow 212\text{Mn}^{2+} + 106\text{CO}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
R4	$\text{OM} + 424\text{FeOOH} + 848\text{H}^+ \rightarrow 424\text{Fe}^{2+} + 106\text{CO}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
R5	$\text{OM} + 53\text{H}_2\text{SO}_4 \rightarrow 53\text{H}_2\text{S} + 106\text{CO}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
R6	$\text{OM} \rightarrow 53\text{CO}_2 + 53\text{CH}_4 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
R7	$\text{CH}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{S}$
R8 ^c	$\text{OM} + \frac{424}{15}\text{FeOOH} + \frac{848}{15}\text{H}_2\text{SO}_4 \rightarrow 106\text{CO}_2 + \frac{424}{15}\text{FeS}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$

^aModified after *Canfield et al.* [1993a], *Chen and Wang* [1999], and *Van Cappellen and Wang* [1996].

^bOM in R2–R8 represents organic matter that has the Redfield elemental composition (R1).

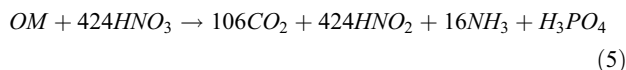
^cR8 is coupled sulfate and iron reduction that produces alkalinity and pyrite.

upward diffusing ammonia, which is produced in anaerobic remineralization reactions in sediments [*Hulth et al.*, 2005; *Middelburg et al.*, 1996]. Sedimentary nitrification is indicated by either subsurface maxima of nitrate profiles [e.g., *Burdige*, 2006] or benthic nitrate efflux to overlying waters [*Berelson et al.*, 2003]. Similarly, another type of coupling, i.e., coupled nitrogen fixation-nitrification-denitrification on a much larger spatial scale does not lead to a system-wide alkalinity gain either (see section 3 for details).

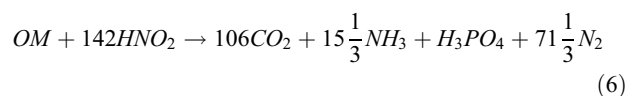
[11] In light of the above discussion, it is clear that using overall denitrification rates, i.e., either modeled or field-measured values [e.g., *Cornwell et al.*, 1999; *Middelburg et al.*, 1996], as a proxy to calculate alkalinity production would exaggerate its significance. Thus differentiating nitrate sources that supply the denitrification process is particularly important if we are to determine the significance of ocean margin denitrification on global alkalinity budget.

[12] During the last decade, increasing evidence has been suggesting that anaerobic ammonia oxidation (or anammox), in addition to the canonical denitrification, plays an important role in oceanic nitrogen cycle in removing fixed nitrogen, especially in the OMZs near the continental margins [*Brandes et al.*, 2007; *Hulth et al.*, 2005; *Kuypers et al.*, 2005; *Lam et al.*, 2009; *Thamdrup and Dalsgaard*, 2002]. However, how anammox affects alkalinity is not clear.

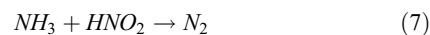
[13] The anammox reaction needs a nitrite (i.e., NO_2^-) source. One major nitrite production pathway is through the so-called “dissimilatory nitrate reduction to nitrite” or DNRN process [*Hulth et al.*, 2005; *Koeve and Kähler*, 2010; *Lam et al.*, 2009]. Assuming the substrate organic matter has the Redfield composition (i.e., OM represents $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$; also see Table 1), we can write the DNRN reaction as:



[14] Nitrite produced in Reaction (5) can react with organic matter further (Reaction (6)) which, when combined together with Reaction (5), is equivalent to the canonical denitrification (e.g., R2 in Table 1):



[15] On the other hand, for the anammox reaction pathway, nitrite reacts with ammonia and this reaction produces N_2 directly (Reaction (7)):



[16] From Reactions (5)–(7), if a system receives *net* nitrate input from an external source, then there is a production of alkalinity that equals to the influx of nitrate (for brevity, let us first ignore the small contribution of phosphoric acids). Note nitrite is an intermediate reactant thus it does not cause net alkalinity change from the system-wide perspective (similar to ammonia, see above).

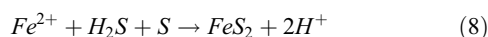
[17] The other nitrite source is aerobic oxidation of ammonia [*Hulth et al.*, 2005; *Lam et al.*, 2009], and ammonia is the product of ammonification through organic matter decomposition. In this case, subsequent anammox in conjunction with ammonia oxidation is equivalent to coupled nitrification/denitrification from a mass balance point of view. Therefore, this coupled process does not lead to net alkalinity change.

[18] In essence, despite the fact that anammox is an important metabolic pathway in the oceanic nitrogen cycle, it can still be placed in the context of denitrification when its influence on alkalinity budget is considered, because the ultimate alkalinity production relies on an external nitrate source. Therefore in the following discussion in examining the effect of assumed steady state nitrogen cycle on oceanic alkalinity budget (section 3), anammox will not be listed as a separate process.

[19] Other than aerobic remineralization and denitrification, all anaerobic remineralization pathways apparently produce alkalinity according to reactions in Table 1. Anaerobic remineralization reactions are important in recycling organic matter in ocean margin sediments, where abundant organic carbon input leads to fast oxygen depletion within millimeters of the sediment-water interface [*Cai and Sayles*, 1996; *Reimers et al.*, 1992]. Sedimentary organic matter remineralization generally follows the diagenetic reaction sequence [e.g., *Burdige*, 2006]. However, when it comes to terminal electron acceptors, O_2 is usually the dominant or ultimate oxidizer when bottom seawater is well-oxygenated even though anaerobic organic carbon remineralization reactions occur at sediment depth [*Canfield et al.*, 1993b; *Martin and Sayles*, 2004], hence both sulfur and the metal

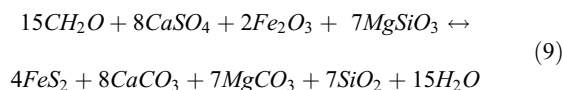
species are recycled many times before they can be preserved in sediments and enter the long-term geological cycle [Canfield *et al.*, 1993a, 1993b; Jørgensen, 1977, 1982]. Therefore, only a net loss (or burial) of reduced compounds can be counted toward alkalinity production.

[20] Reduction of metal (mostly iron and manganese) oxides produces alkalinity according to R3 and R4 (Table 1). However, when accounting for net alkalinity gain, we need to consider not only the reduction reactions themselves, but to take into account the fate of the reduced species (i.e., Fe^{2+} and Mn^{2+}). Neither Fe^{2+} nor Mn^{2+} is accumulating in significant amounts in oceanic waters, therefore, eventual preservation of these metals requires that both ions are precipitated and preserved in the sediments. In the case of iron, reduced iron (after R4) is preserved as pyrite. Because pyrite is thermodynamically stable, it is considered the permanent sink for both iron and sulfur on early diagenetic time scales [Chanton and Martens, 1987; Hammond *et al.*, 1999; Jørgensen, 1977; Lin and Morse, 1991; Raiswell and Canfield, 1998; Rickard and Luther, 2007]. Formation of pyrite leads to the production of acid, which cancels alkalinity produced in R4 (Table 1; see the theoretical coupled reaction in R8).



Therefore, net alkalinity production due to iron reduction and further reduced iron preservation must be close to nil. Note in Reaction (8), sulfur can be considered as a product of incomplete sulfate reduction. Similarly, reduced manganese (e.g., Mn(II)) is also predominantly present in solid form in marine sediments [Burdige, 1993] despite the fact that initial reduction of MnO_2 produces Mn^{2+} and alkalinity (R3, Table 1).

[21] Kempe [1990] proposed perhaps the most direct basin-scale linkage between anaerobic remineralization and carbonate alkalinity production. In his work, Kempe [1990] suggested that alkalinity production by anaerobic remineralization in enclosed anoxic basins leads to the occurrence of carbonate facies found in ancient epicontinental seas. Similar observation was made in some euxinic basins such as the Baltic Sea, where water exchange with the open ocean is restricted. Water column buildup of alkalinity caused by pyrite formation facilitates carbonate precipitation [e.g., Sternbeck and Sohlenius, 1997]. In addition, Berner [1984] proposed a coupled anaerobic remineralization and carbonate production reaction, in which he wrote a simplified equation (Reaction (9)) to describe the global redox balance between sulfate and pyrite in maintaining constant atmospheric O_2 throughout the Phanerozoic:



Reaction (9) reflects a coupled process between continental crust (iron and silicate minerals) weathering and subsequent transformation of the redox couples (both carbon and sulfur). Although these studies dealt with this issue on different spatial and time scales, for example, Berner's work focused on rather global and long time scale changes as opposed to the other two regional studies, the underlying relationship

between net sulfate reduction (i.e., pyrite formation) and alkalinity production (i.e., carbonate precipitation) is essentially the same. Again according to this Reaction (9), iron reduction above does not lead to net alkalinity (or carbonate) production.

[22] Therefore, based on the above discussion, it is clear that denitrification (here includes anammox) based on net nitrate input (R2, Table 1) and pyrite burial associated with *net* sulfate reduction (R5, but not Fe/Mn reduction) are the only processes that can contribute to net alkalinity gain in the oceanic environment.

[23] It is worth noting that authigenic carbonate precipitation caused by pore water saturation increase, as a result of anaerobic alkalinity production (especially anaerobic methane oxidation, i.e., R7), could consume alkalinity, for example,



where M represents metal ions such as Fe^{2+} , Mn^{2+} , Ca^{2+} and Mg^{2+} . Note in essence, Reaction (10) is equivalent to Reaction (8) in terms of describing alkalinity consumption (i.e., acid produced in Reaction (8) also consumes alkalinity) following the precipitation of reduced Fe/Mn. If pore water alkalinity were completely converted to authigenic carbonate, then there would be no net alkalinity efflux to the overlying water column. However, this scenario is likely unrealistic based on field observations, i.e., researchers have observed net alkalinity gradients at the sediment-water interface of anoxic sites, which eventually lead to alkalinity export [e.g., Berelson *et al.*, 2003]. In other cases though, pore water calcium depletions at depth within the sediment sometimes do indicate carbonate precipitation [Berelson *et al.*, 2005; Mucci *et al.*, 2000]. The reason that authigenic carbonate production does not occur ubiquitously in marine sediments probably is due to the inhibiting effect of organic carbon or, the lack of abundant carbonate nuclei [Berner *et al.*, 1970].

[24] Under certain circumstances, extensive pyrite formation together with the occurrence of authigenic carbonate has been observed in many petroleum seep areas that spread around the global ocean margins [Chen *et al.*, 2007; Sassen *et al.*, 2004; Snyder *et al.*, 2007; Stakes *et al.*, 1999; van Dongen *et al.*, 2007]. However, this potential alkalinity (carbonate) production is not associated with burial of modern carbon, but anaerobic remineralization of fossil carbon. Hence it is independent of alkalinity production/pyrite burial occurring in modern anoxic sediments, and it should be separated from ocean margin alkalinity production in this paper. This alkalinity source could potentially contribute to the global alkalinity budget and needs to be further quantified [Snyder *et al.*, 2007]. However, due to limited understanding with respect to the magnitudes of anaerobic hydrocarbon oxidation and associated carbonate deposition in this type of environment, we choose not to discuss this issue further.

3. Alkalinity Generation Through Net Denitrification

[25] In the modeling work by Middelburg *et al.* [1996], it was estimated that the global rate of denitrification in marine sediments is on the order of 230–285 Tg N yr^{-1} , of which

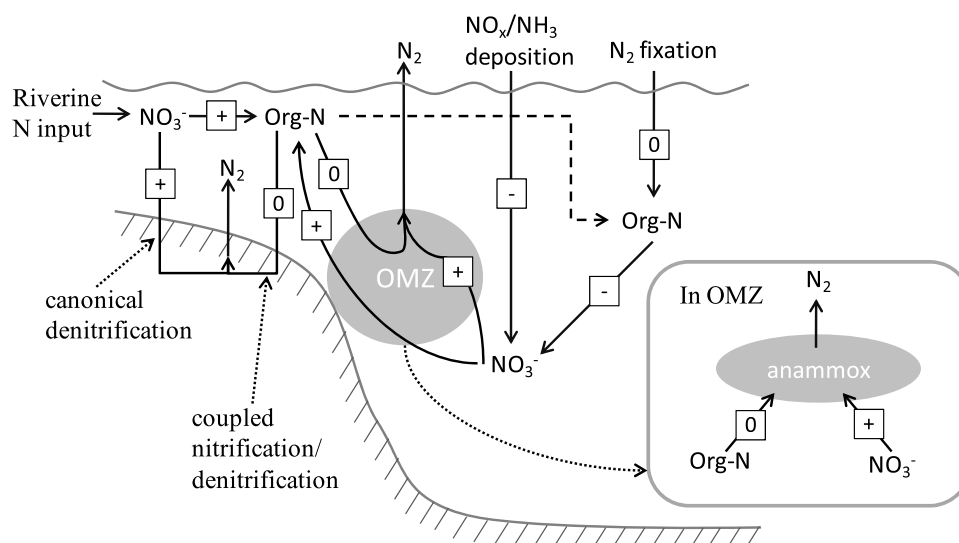


Figure 1. Schematic representation of the role of global ocean nitrogen cycle on alkalinity budget. Plus (+) and minus (−) signs represent net production and consumption of alkalinity in corresponding processes, respectively. Zero (0) indicates no net alkalinity change. The inset summarizes the effect of the anammox process on alkalinity production in the oxygen minimum zone (OMZ). Note anammox does not dominate fixed nitrogen removal in all OMZs [e.g., Ward *et al.*, 2009]. See text for a detailed discussion.

~100 Tg N yr^{−1} occurs in continental shelf sediments. This global denitrification rate agrees well with studies that utilized nitrogen stable isotope mass balance [Brandes and Devol, 2002]. Continental shelf denitrification, however, was recently revised upward to 250 Tg yr^{−1}, which includes 166 Tg N yr^{−1} in nonpolar shelf sediments, and 45 Tg N yr^{−1} in polar sediments [Seitzinger *et al.*, 2006]. The latter estimate is in line with the estimates in the reviews by Codispoti [2007] and Galloway *et al.* [2004]. Furthermore, Seitzinger *et al.* [2006] attributed the above mentioned 211 Tg N yr^{−1} (i.e., 166 + 45) to coupled nitrification/denitrification, while sedimentary denitrification using bottom water nitrate as its nitrate source (i.e., through net nitrate input) is only ~40 Tg N yr^{−1}.

[26] On the other hand, current views on the Holocene global oceanic nitrogen cycle are represented by two schools of thought, i.e., either nitrogen fixation and denitrification are approximately balancing each other [Brandes and Devol, 2002; Brandes *et al.*, 2007; Capone and Knapp, 2007; Deutsch *et al.*, 2007], or there is an apparent nitrogen fixation deficiency (as much as 200 Tg N yr^{−1}) due to current understanding that global ocean denitrification rate is apparently greater than that of nitrogen fixation [Codispoti, 2007; Hulth *et al.*, 2005]. Ongoing investigations are still revealing novel oceanic nitrogen fixers [Moisander *et al.*, 2010], which may narrow the gap between the two contrasting views of global nitrogen cycle. While a complete discussion of global nitrogen mass balance is beyond the scope of this work, we emphasize that nitrogen fixation followed by aerobic remineralization is an acid-producing process [Wolf-Gladrow *et al.*, 2007] as shown in Reactions (3)–(4). Therefore if the oceanic nitrogen cycle maintains a steady state, which we choose as an assumption in our present discussion, the overall effect of alkalinity production through

denitrification may not be significant on the global scale (Figure 1).

[27] In light of the above discussion, we can therefore calculate alkalinity production through denitrification reaction from an “out-of-box” perspective. In this approach, again if we assume a homeostatic oceanic nitrogen cycle on the global scale, i.e., oceanic nitrate input is balanced by N₂ loss through denitrification and anammox, then the difference between the source and sink terms, i.e., nitrogen fixation caused nitrate input and denitrification/anammox induced nitrate removal (in the form of N₂ gas), has to be the influx of terrigenous nitrate, which is transported via rivers and to a lesser extent, atmospheric deposition. Seitzinger *et al.* [2006] estimated that denitrification consumes 8, 46, and 25 Tg N yr^{−1} of land-based nitrogen (including both organic and inorganic) in estuaries, continental shelves, and ocean oxygen minimum zones (OMZ), respectively, although each value has a near 100% uncertainty. In comparison, Galloway *et al.* [2004] estimated that rivers export 48 Tg N yr^{−1}, of which 21 Tg N yr^{−1} is inorganic nitrogen. Their total riverine input is similar to the value (8 + 46 Tg N yr^{−1}) estimated by Seitzinger *et al.* [2006]. Based on the fact that global shelf total denitrification exceeds 200 Tg N yr^{−1} [Seitzinger *et al.*, 2006], it is safe to assume that all river-delivered fixed nitrogen is consumed via denitrification within continental shelves. Therefore the maximum denitrification that can generate alkalinity, in a net sense, can be based on the assumption that all 21 Tg yr^{−1} (or 1.5 Tmol yr^{−1}) of inorganic nitrogen is in the form of nitrate. Then denitrification using this net nitrate input produces an alkalinity at a rate of 1.5 Tmol yr^{−1} from the reaction stoichiometry in R2 (Table 1). In addition, Seitzinger *et al.* [2006] assumed that all atmospheric deposition of land-based fixed nitrogen (25 Tg N yr^{−1}, see above) is denitrified in the OMZs. However, despite their short-term acidifying effect in the

upper ocean, i.e., ammonia oxidation and dissolution of NO_x would initially cause slight acidification (together with sulfuric acid deposition, they cause a few percent of acidification of that induced by anthropogenic CO_2 input [Bates and Peters, 2007; Doney *et al.*, 2007]), if the resulting nitric acid is ultimately converted back to N_2 , neither form of atmospheric nitrogen deposition would cause net alkalinity change to the global ocean (Figure 1).

[28] Although with a potentially large uncertainty, which mostly stems from the uncertain on the state of oceanic nitrogen cycle, our estimate of alkalinity generation due to nitrate loss through denitrification (here also includes anammox) is far less important than previously thought [Thomas *et al.*, 2009]. However, on local scales excess alkalinity may be produced due to external nitrate input from riverine and upwelled slope water sources, even though their global significance likely remains small (see section 6).

4. Alkalinity Generation Through Continental Shelf Pyrite Burial

[29] In the literature, global oceanic pyrite burial rates in river deltaic and continental shelf siliciclastic sediments have been historically derived using an indirect means – the sedimentary C/S ratio. This approach stems from the near constant sedimentary C/S ratio observed in both marine sediments under oxic waters and ancient shales that are of oceanic origin (weight ratio of 2.8 ± 0.8 , or molar ratio of 7.5 ± 2.1 [see Berner, 1982]). Given the fact that there have been more studies on organic carbon preservation than on pyrite burial [Berner, 1982; Burdige, 2007; Hedges and Keil, 1995; Lin and Morse, 1991; Volkov and Rozanov, 1983], this approach should yield a more conclusive result than that obtained directly from global pyrite burial studies.

[30] Over the past three decades, significant progress has been made on quantifying organic carbon burial rates in marine sediments. In the meantime, more extensive knowledge has also been obtained regarding burial locations of sedimentary organic carbon. Both factors (burial rate and location) will determine the extent of pyrite burial and associated benthic alkalinity production in continental shelves.

[31] Berner [1982] suggested that most organic carbon burial occurs in river deltas and continental shelves at a rate of 110 Tg C yr^{-1} . In a later synthesis, Berner [1989] maintained the same conclusion regarding burial locations although he revised the burial rate slightly upward to 114 Tg C yr^{-1} . This value reflects burial rates of 104 Tg C yr^{-1} in deltaic-shelf sediments and 10 Tg C yr^{-1} in upwelling zones, respectively. Later, Hedges and Keil [1995] suggested that 70 Tg C yr^{-1} burial occurs in deltaic sediments. At the same time, after accounting for higher organic content in sediments of nondeltaic shelves and upper continental slopes than that in Berner's estimate (i.e., 1.5% versus 0.7%), they proposed a burial rate of 68 Tg C yr^{-1} in these environments. Then taking the same 10 Tg C yr^{-1} burial in upwelling zones, Hedges and Keil [1995] revised the organic carbon burial upward to 148 Tg C yr^{-1} . This estimate includes organic carbon burial rate in upper continental slope, so actual organic carbon burial rate within continental shelves should be smaller than this value.

[32] More recently, Burdige [2007] differentiated the types of sediments within the 200 m water depth based on their organic carbon content, i.e., sandy and muddy sediments account for 70% and 30% of total shelf area, respectively. These two types of sediments have different organic carbon burial efficiency ($\text{BE} = \text{OC}_{\text{burial}}/\text{OC}_{\text{input}} \times 100\%$). BE values in sandy and in muddy sediments are 1% and 30%, respectively. Using depth integrated organic carbon remineralization rates, Burdige [2007] calculated that organic carbon burial rate is 152 Tg C yr^{-1} . In addition, organic carbon burial rate in the 200–1000 m depth range is estimated to be 70 Tg C yr^{-1} . This then puts the global organic carbon burial rate in deltaic/shelf/continental slope areas as 222 Tg C yr^{-1} , which agrees well with an earlier estimate (232 Tg C yr^{-1}) by Volkov and Rozanov [1983].

[33] Most people consider deltaic and shelf sediments as the major organic carbon burial sites [Berner, 1982, 1989; Burdige, 2007; Hedges and Keil, 1995]. Another view, however, suggests that continental shelves cannot be significant modern-day organic carbon burial locations. Instead, organic carbon originally deposited on continental shelves is finally removed into continental slopes and further oceanward locations (canyons and deep-sea fans [de Haas *et al.*, 2002; Masson *et al.*, 2010]). Furthermore, using sediment size and net sedimentation rates, de Haas *et al.* [2002] suggested that most organic carbon deposition in nearshore environments is associated with fine-grained sediments that are transported via river discharge. This conclusion appears to be consistent with the conclusion regarding high BE values in muddy sediments [Burdige, 2007].

[34] Without having to resolve the contentious issue regarding the exact organic carbon burial locations, from the perspective of alkalinity production, it is the organic carbon burial in both deltaic and nondeltaic continental shelves that we should focus on. Such burial should be associated with burial of pyrite (although see section 2 for pyrite production in cold seep environments), which leads to alkalinity production that contributes to the oceanic alkalinity budget. Therefore, it appears reasonable that the estimate of Berner [1982, 1989] ($\sim 110 \text{ Tg C yr}^{-1}$) can be used as a lower bound, whereas Burdige's [2007] estimate can be used as an upper bound to bracket the range of organic carbon preservation and to predict the alkalinity production rate. Using these two boundary values (110 and 150 Tg C yr^{-1}) and the C/S weight ratio of 2.8, we can calculate that pyrite burial rate in continental shelves is in the range of 39 – 54 Tg S yr^{-1} (or 1.2 – 1.7 Tmol yr^{-1}), which leads to an alkalinity production rate of 2.4 – 3.3 Tmol yr^{-1} according to the reaction stoichiometry in R8 (Table 1).

5. Pyrite Burial in Sediments of Coastal Vegetated Habitats

[35] Conventional view suggests that continental shelves (mainly deltaic and shelf) and slopes are major organic carbon depositional environments [Berner, 1982; Burdige, 2007; de Haas *et al.*, 2002; Hedges and Keil, 1995]. Recently, however, Duarte *et al.* [2005] proposed that sediments in vegetated habitats, including salt marshes, mangroves, and seagrass meadows, constitute a missing reservoir in global carbon budgetary estimations. Their estimated organic carbon burial rate (111 Tg yr^{-1}) in these environ-

Table 2. Sedimentary C/S Weight Ratio in Salt Marsh Sediments

C/S Ratio	OC (%)	Reference
4.1–74.8 ^a	4.8–38.9	Giblin [1988]
3.5–6.3	0.8–7.1	Oenema [1990]
8.4–39.0	8–17	Giblin [1988]
3.3	5.0	Lord and Church [1983]
3.4–7.0	3.4–4.5	Borrego et al. [1998]

^aValues are from deep core depths (15–20 cm) with an assumption that these values represent buried C/S ratios.

ments is similar to the value obtained for continental shelves based on oceanic literature (see above).

[36] In their tabulation, *Duarte et al.* [2005, Table 1] indicated that global mangroves and salt marsh areas are 0.2×10^{12} and 0.4×10^{12} m², respectively. However, their calculations double-counted the mangrove area because the so-called marsh area (0.38×10^{12} m²; note *Duarte et al.* used 0.4×10^{12} m²) originally summarized by *Woodwell et al.* [1973] actually includes both mangrove forests and salt marshes. If we use the average organic carbon burial rate of 145 g C m⁻² yr⁻¹ given by *Chmura et al.* [2003] and global total mangrove and salt marsh area of 0.38×10^{12} m², organic carbon burial rate in these two types of environments is 55 Tg C yr⁻¹. It is worth noting that the organic carbon burial rate given by *Chmura et al.* [2003] possibly represents an upper bound, because this rate is mostly derived from mangrove-dominated sediments. This value is about three times that observed in three Georgian estuaries in the U.S. that are marsh-dominated [*Loomis and Craft*, 2010]. If we take an area-averaged organic carbon burial rate of 57 g C m⁻² yr⁻¹ after considering different marsh types in these estuaries (freshwater versus salt marshes) [*Cai*, 2011], total organic carbon burial on the global scale is only 22 Tg C yr⁻¹. Then incorporating the 27 Tg C yr⁻¹ organic carbon burial of seagrass carbon [*Duarte et al.*,

2005], we can reach a global organic carbon burial rate of 49–82 Tg C yr⁻¹ in all vegetated sediments (mangroves, salt marshes, and seagrass), which is much smaller than the value (111 Tg yr⁻¹) given by *Duarte et al.* [2005]. However, two more recent papers have given much higher carbon preservation rates in seagrass meadows alone [*Duarte et al.*, 2010; *Kennedy et al.*, 2010].

[37] Due to high primary productivity and low salinity (brackish) in these habitats (especially in salt marshes), sedimentary C/S ratios exhibit a wide range but the values are generally much higher than those in common marine sediments (Table 2). Elevated C/S ratios in these environments can be attributed to either low sulfate supply from seawater in settings that have restricted water exchange (cf. freshwater environment [*Berner and Raiswell*, 1984]) or iron limitation [*Morse and Berner*, 1995]. Because of the high heterogeneity of these vegetated habitats, it is difficult to deduce a well-constrained pyrite burial rate using organic carbon burial rate. Nevertheless, for a back-of-the-envelope estimate, assuming a range of C/S weight ratio of 4.5–26.1 based on the arithmetic means of the C/S ranges from previous studies (Table 2), we estimate a pyrite burial rate of 1.9–18 Tg yr⁻¹ (or 0.1–0.6 Tmol S yr⁻¹) based on 49–82 Tg yr⁻¹ organic carbon burial rate. This amount of pyrite burial would lead to alkalinity production of 0.1–1.1 Tmol yr⁻¹.

6. Discussion

[38] Based on denitrification and pyrite burial, total anaerobic remineralization-induced alkalinity production is on the order of 4–5 Tmol yr⁻¹ (1.5 Tmol yr⁻¹ from denitrification, 2.5–3.3 Tmol yr⁻¹ from pyrite burial) that contributes to the net global oceanic alkalinity budget (Figure 2). In addition, although organic carbon preservation in coastal vegetated sediments represents an unconventional view in the context of the global carbon cycle, if taking this into

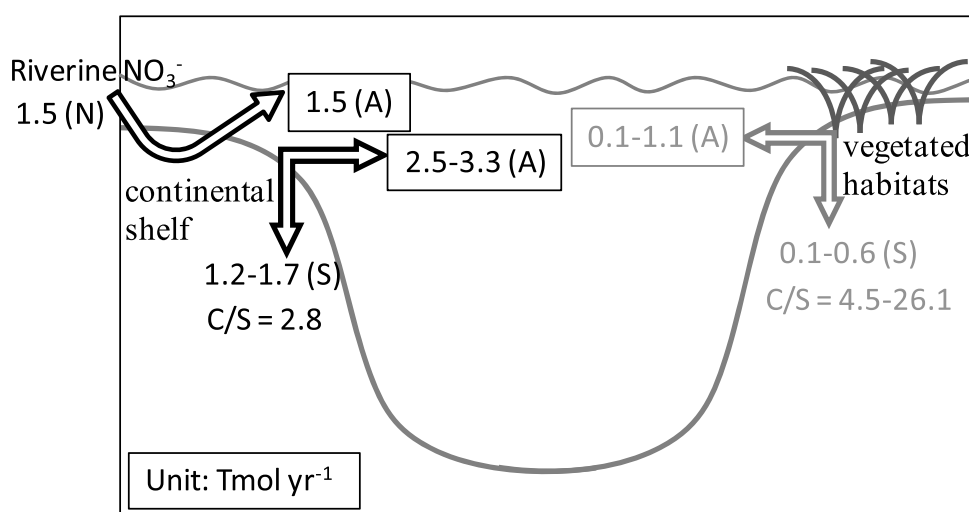


Figure 2. A summary of ocean margin anaerobic processes on global oceanic alkalinity budget. The notations in the parentheses represent nitrogen (N), pyrite sulfur (S), and alkalinity (A). Alkalinity production and pyrite burial in coastal vegetated habitats are marked in gray to show the unconventional view of organic carbon preservation there and highlight the uncertainties with the associated pyrite burial. The C/S ratios are based on weight.

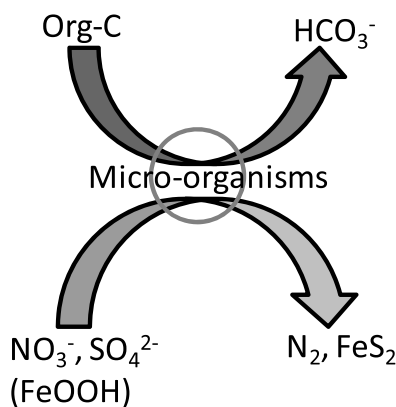


Figure 3. A schematic illustration of the charge transfer during different anaerobic remineralization pathways; microorganisms play an important role in these reactions.

consideration, another $0.1\text{--}1.1\text{ Tmol yr}^{-1}$ alkalinity may be produced via pyrite burial there. Then, the overall alkalinity production rate would increase to $\sim 4\text{--}6\text{ Tmol yr}^{-1}$. To put this in perspective, global riverine alkalinity input (in the form of bicarbonate) ranges between 32 and 36 Tmol yr^{-1} [Berner *et al.*, 1983; Cai *et al.*, 2008; Lerman and Mackenzie, 2005], and global ocean alkalinity production has a range of $42\text{--}133\text{ Tmol yr}^{-1}$ [Berelson *et al.*, 2007]. In another word, net alkalinity production through the anaerobic processes in the ocean margins only accounts for less than 15% of the global oceanic value.

[39] Clearly, our estimate of benthic alkalinity production is much (at least 60%) lower than the estimates ($16\text{--}31\text{ Tmol yr}^{-1}$) of Chen [2002]. Furthermore, Thomas *et al.* [2009] suggested that alkalinity production from denitrification in continental shelves alone would have an alkalinity production rate of 18 Tmol yr^{-1} based on denitrification rate of 250 Tg N yr^{-1} . In fact, this gross denitrification actually includes $>80\%$ of coupled nitrification/denitrification [Seitzinger *et al.*, 2006]. Moreover, they did not consider the temporal/spatial coupling of the nitrogen cycle either.

[40] From the global nitrogen mass balance point of view (Figure 1), excess alkalinity may be generated on regional scales, through the coupling of “new” production (i.e., primary production using upwelled open ocean nitrate) and denitrification. However, pelagic nitrogen fixation and subsequent nitrification would produce nitrate and proton that offsets this alkalinity production in shelf areas [Wolf-Gladrow *et al.*, 2007]. Here, we note that such compensation largely depends on the assumption that the global ocean nitrogen cycle is at steady state. Therefore, if both denitrification (including anammox in the OMZs) and nitrogen fixation occur in a spatially and temporally coupled way, as suggested by Deutsch *et al.* [2007] and Capone and Knapp [2007], potentially even on regional scales this type of alkalinity production may be canceled. Therefore, other than the small portion of denitrification based on net external nitrate input, i.e., from rivers, shelf denitrification has little or no global impact on oceanic alkalinity budget per se.

[41] Regarding sulfate reduction and subsequent pyrite burial, it is conceptually inappropriate to use the gross anaerobic remineralization rate measured *ex situ* to infer the rate of alkalinity production. For example, Chen and Wang

[1999] calculated that a significant part of alkalinity production based on extrapolating the sulfate reduction rate reported by Huang and Lin [1995], who used ^{35}S to determine gross sulfate reduction rates through a closed-system incubation technique. However, the sediment C/S weight ratio (~ 3) at sediment depth in this area agrees with the value of 2.8 observed in common marine sediments, which indicates that our method of calculating alkalinity production using the constant C/S ratio should apply. Consequently, based on the recent summary that organic carbon burial rate is 7.4 Tg C yr^{-1} in the East China Sea continental shelf sediments [Deng *et al.*, 2006], pyrite sulfur burial rate is calculated to be 2.6 Tg S yr^{-1} (0.08 Tmol yr^{-1}), and alkalinity production from this pyrite burial is only 0.16 Tmol yr^{-1} . Clearly, this alkalinity production is far less than the estimated value given by Chen and Wang [1999] ($3.9 \pm 3.9\text{ Tmol yr}^{-1}$). Furthermore, neither iron nor manganese reduction should contribute to a net alkalinity gain (section 2), contrary to what Chen and Wang [1999] suggested.

[42] Pyrite burial is limited by the availability of organic carbon rather than iron in many continental shelf sediments [Huang and Lin, 1995; Lin and Morse, 1991; Morse and Berner, 1995; Raiswell and Canfield, 1998]. Therefore, future increases in agricultural fertilizer usage and land use change would enhance riverine export of fixed nitrogen [Yan *et al.*, 2010], which could promote continental shelf primary production and subsequent organic carbon burial. This feedback mechanism may lead to enhanced pyrite burial and thus the associated alkalinity production. On the other hand, the presence of river dams may also have profound ecological impacts, including decreased freshwater input into receiving shelf that could cause less cross-shelf water exchange/upwelling [e.g., Chen, 2000] and altered nutrient ratios in river waters [Gong *et al.*, 2006], both of which could lead to nutrient limitation, hence reduce continental shelf primary production. Therefore, organic carbon production and preservation in these areas will depend on the interplay between these two anthropogenic factors.

[43] Regarding vegetated sediments, a caveat needs to be pointed out as recent loss of coastal habitats [Duarte *et al.*, 2005, 2010; Kennedy *et al.*, 2010; Talaue-McManus, 2010] could be reducing the burial of organic carbon (and pyrite) in the coastal habitats, which would reduce corresponding alkalinity production. Pyrite burial in marine sediments can be considered as a long (geological) time preservation and it sustains alkalinity contribution to the oceanic environment. In contrast, if the accretion of coastal habitats cannot keep up with the sea level rise (a nonsteady state) due to recent climate change, continuous loss of coastal habitats and associated sedimentary organic carbon and pyrite loss may cause net acid production, through pyrite reoxidation after these habitats are inundated and washed offshore. Unfortunately, limited by the sporadic studies involved in this type of environment [e.g., Chmura *et al.*, 2003], it is not yet possible to draw a conclusion on this issue and future studies clearly are needed.

[44] Upon closer examination of these anaerobic processes (Table 1), we propose that anaerobic alkalinity production can be viewed as an anion charge transfer process along with these redox reactions (Figure 3). In this simplified view, bicarbonate (alkalinity) is produced as organic carbon is oxidized by land-derived nitrate and sulfate, and

iron/manganese oxides (R2, R4, and R5, Table 1). Land-derived nitrate first originated from natural nitrogen fixation prior to the anthropocene, but more recently industrial synthesis has been playing an increasingly important role in total nitrogen fixation [Galloway *et al.*, 2008]. In the mean time, sulfate, iron and manganese oxides are derived from continental weathering. Now it becomes clear that from the perspective of charge balance: since both manganese and iron oxides are delivered to the continental shelves in uncharged solid (or colloidal) form and subsequent preservation also involves uncharged solid form, there is no net charge production so that alkalinity production proposed in previous studies [e.g., Chen, 2002] is rather a transient process. Therefore, our anion charge transfer view is consistent with the alkalinity balance equation (equations (1)–(2)) since the presence of metal ions is transient in the redox reactions and thus can be omitted. Taken together, through net denitrification and net sulfate reduction with a permanent loss of N_2 and pyrite, nitrate and sulfate transfer their negative charge to HCO_3^- by oxidizing organic carbon (Table 1). In other words, these processes produce the anion (or conjugate base) of a weak acid (H_2CO_3), which contributes to alkalinity, out of the anions of strong acids (HNO_3 and H_2SO_4), which do not.

7. Summary

[45] Based on our literature survey and analysis of known reaction stoichiometry, we conclude that the *net* alkalinity production from anaerobic processes in global ocean margin areas is on the order of $4\text{--}5\text{ Tmol yr}^{-1}$, which is significantly less than previous estimates. Even adding an extra source of alkalinity due to pyrite burial in coastal vegetated sediments, despite its possible short-term significance, the total alkalinity production is only $\sim 4\text{--}6\text{ Tmol yr}^{-1}$ (Figure 2). Previous studies have derived much higher values by either neglecting the significance of internal nitrogen cycling, such as coupled nitrification/denitrification, or inferring alkalinity production in a conceptually inappropriate way. This type of alkalinity production can be viewed as an anion charge transfer process between the oxidative anions (nitrate, sulfate) and CO_2 , through organic carbon remineralization. Therefore if the entire ocean as a whole system is examined, only net loss of external nitrate and sulfate through N_2 gas evasion and sediment pyrite burial, respectively, can be considered as the actual processes that complete this charge transfer.

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