Chemoautotrophy in the ocean

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[1] Organic matter recycling releases ammonium, and under anoxic conditions, other reduced metabolites that can be used by chemoautotrophs to fix inorganic carbon. Here I present an estimate for the global rate of oceanic carbon fixation by chemoautotrophs (0.77 Pg C y^{-1}). Near-shore and shelf sediments (0.29 Pg C y^{-1}) and nitrifiers in the euphotic zone (0.29 Pg C y^{-1}) and the dark ocean (0.11 Pg C y^{-1}) are the most important contributors. This input of new organic carbon to the ocean is similar to that supplied by world-rivers and eventually buried in oceanic sediments. Chemoautotrophy driven by organic carbon recycling is globally more important than that fuelled by water-rock interactions and hydrothermal vent systems. **Citation:** Middelburg, J. J. (2011), Chemoautotrophy in the ocean, *Geophys. Res. Lett.*, *38*, L24604, doi:10.1029/2011GL049725.

1. Introduction

[2] Ecosystems on land and in the ocean are highly efficient in the recycling of energy and matter. The net annual primary production by terrestrial ecosystems is about 56 Pg C y^{-1} [*Field et al.*, 1998] and most of the carbon fixed is recycled because net carbon burial in terrestrial systems (1–4 Pg C y^{-1} [*Cole et al.*, 2007]) and export to the ocean via rivers (0.4–0.5 Pg C y^{-1} [*Cole et al.*, 2007]) are relatively small. Similarly, marine primary production has been estimated at about 48.5 to 54 Pg C y^{-1} [*Field et al.*, 1998; *Dunne et al.*, 2007] and only 0.2 to 0.79 Pg C y^{-1} (~1%) is buried in marine sediments [*Burdige*, 2007; *Duarte et al.*, 2005; *Dunne et al.*, 2007], implying that close to all net marine primary production is recycled. Heterotrophs efficiently recycle organic matter because they depend on the energy in organic matter. However, heterotrophs cannot use all organic energy because some is shunted into metabolites such as ammonium, and under anoxic conditions into reduced substances such as sulfide. These reduced inorganic compounds are used by chemo(litho) autotrophs to obtain energy for inorganic carbon fixation [*Howarth*, 1984; *Raven*, 2009]. In this paper, I present a global estimate of carbon fixation by chemoautotrophs in the ocean and identify coastal sediments and nitrifiers in ocean surface and deep waters as dominant contributors.

2. Methods

[3] Following a recent synthesis of organic carbon cycling in the ocean [*Dunne et al.*, 2007], the ocean is divided by depth regime: near-shore (<50 m), shelf (50–200 m), slope (200–2000 m) and open ocean (>2000 m) with surface areas of 0.71, 0.95, 2.24 and 31.07 × 10^{13} m^2. *Dunne et al.* [2007] reported internally consistent estimates for net primary production, organic matter export, respiration in the euphotic zone, the dark ocean and the sediments, and organic burial for these oceanic environments. These carbon flows provided the basis for our estimates for chemoautotrophic carbon fixation in the euphotic zone, in the dark ocean and marine sediments of near-shore, shelf, slope and open ocean settings (Figure 1 and Table 1, the auxiliary material provides more details on calculations).[1]

[4] Chemoautotrophic carbon fixation in the euphotic layer and dark ocean waters is assumed to be restricted to nitrification, the oxidation of ammonium to nitrate. Dark ocean carbon fixation due to nitrification is calculated by dividing the dark ocean respiration with the Redfield C:N ratio (6.6) and assuming one mole of carbon dioxide is fixed per 10 mole of ammonium oxidized [*Tijhuis et al.*, 1993; *Wuchter et al.*, 2006]. Oxygen minimum zones are not explicitly resolved in this study, but are implicitly included with respect to anaerobic oxidation of ammonium. However, dark-ocean water-column chemoautotrophy fueled by sedimentary or lateral inputs of reduced compounds such as iron and sulfide is not included. Euphotic zone chemoautotrophy is calculated similarly as for the dark ocean, but only a fraction of the ammonium regenerated in the euphotic zone is available for nitrification (0.43), the remaining is consumed by phytoplankton. This fraction has been calculated from data by *Yool et al.* [2007] for their median specific nitrification rate of 0.2 (d^{-1}).

[5] Chemoautotrophy in sediment is mainly supported by re-oxidation of reduced compounds generated during anaerobic processes, with a small contribution by sediment nitrification (0.9 to 1.4% of sediment respiration). Sediment respiration estimates of *Dunne et al.* [2007] are combined with global water-depth resolved nitrification and anaerobic respiration numbers of *Middelburg et al.* [1996] and an ammonium used to carbon fixed ratio of 10 [*Tijhuis et al.*, 1993] and a sulfide oxidized to carbon fixed ratio of 2 [*Dale et al.*, 2010] to arrive at overall efficiencies between 31 and 41% in coastal and ocean margin sediments and 1.5 to 1.7% in deep-sea sediments.

3. Results and Discussion

[6] Global ocean chemoautotrophic carbon fixation totals 0.77 Pg C y^{-1} (Figure 1 and Table 1). Globally about 52% of the chemoautotrophic carbon fixation occurs by nitrifiers in the water column (37% in the euphotic zone and 15% in the dark ocean). Our estimate for inorganic carbon fixation in the dark ocean (0.11 Pg C y^{-1}) is lower than other estimates

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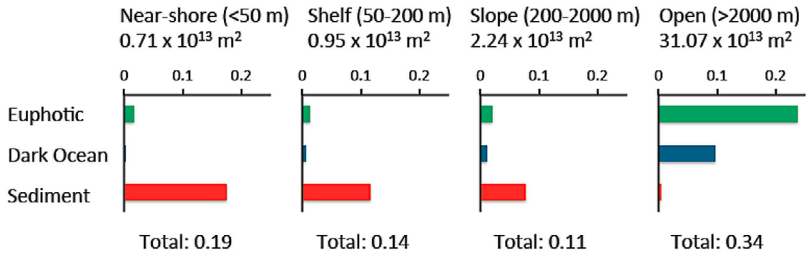

Figure 1. Chemoautotrophy fluxes (Pg C y^{-1}) in the ocean. Total chemoautotrophic carbon fixation rates in the euphotic zone, dark ocean and sediment are 0.29, 0.11 and 0.37 Pg C y^{-1}, respectively.

(0.39 Pg C y^{-1}) [*Wuchter et al.*, 2006] because our estimate is based on a lower global export number (9.6 [*Dunne et al.*, 2007] vs. 26.4 Pg C y^{-1} [*del Giorgio and Duarte*, 2002]). It is also lower than estimates based on extrapolation of measured dark carbon fixation rates that range from 0.8 to 1.1 Pg C y^{-1} [*Reinthaler et al.*, 2010]. Recently, *Swan et al.* [2011] reported widespread potential for chemoautotrophy among bacteria in the dark ocean based on the oxidation of reduced sulfur, carbon monoxide and methane. These energy sources are not included in the calculations implying that our estimate is conservative.

[7] The euphotic zone with its high rates of biogeochemical cycling was identified to be more important than the dark ocean in chemoautotrophic carbon fixation (0.29 vs. 0.11 Pg C y^{-1}). Critical is our assumption that 43% of the ammonium regenerated in the euphotic was available for nitrification [*Yool et al.*, 2007]. If the lower (0.02 d^{-1}) rather than median (0.2 d^{-1}) specific nitrification rate of their sensitivity studies is used, only 16% of the ammonium regenerated is nitrified and euphotic zone carbon fixation by nitrifiers will then total 0.11 Pg C y^{-1}, similar to that in the dark ocean. The mean specific nitrification rate of their dataset was 0.55 d^{-1}, implying that our estimate is conservative.

[8] Chemoautotrophy in sediments is estimated at 0.37 Pg C y^{-1} or about 48% of the total oceanic chemoautotrophic carbon fixation rate. Inorganic carbon fixation is deep-sea sediments is very limited (0.004 Pg y^{-1}) and mainly due to ammonium oxidation. Stable isotope probing with ^{13}C label addition to deep-sea sediments revealed that nitrifiers were the main group incorporating dissolved inorganic carbon [*Guilini et al.*, 2010]. Near-shore, shelf and slope sediments are characterized by shallow oxygen penetration [*Glud*, 2008] and most organic matter mineralization occurs anaerobically [*Jørgensen*, 1982; *Middelburg et al.*, 1996]. Consequently, chemoautotrophy in these settings is primarily fuelled by re-oxidation of reduced metabolites produced during anaerobic degradation of organic matter (primarily sulfides) [*Jørgensen*, 1982; *Howarth*, 1984]. Chemoautotrophic carbon fixation in sediments was estimated by combining sediment respiration rates [*Dunne et al.*, 2007] with re-oxidation efficiencies [*Middelburg et al.*, 1996] to arrive at 0.3 to 0.4 units carbon fixation per unit re-oxidation for near-shore to slope sediments. For instance, near-shore sediment support a chemoautotrophy of 0.175 Pg C y^{-1} based on a global respiration rate of 0.53 Pg C y^{-1} and an overall efficiency of 33%. Coastal and ocean margin sediments receiving high organic carbon loadings are the prime location of chemoautotrophy (0.37 Pg C y^{-1}), because of the combination of high respiration rates and dominantly anoxic conditions. Assuming a more conservative sulfide-oxidized to carbon-fixed ratio of 5 [*Howarth*, 1984] would lower the overall efficiencies in coastal and ocean margins sediments to 10–16% and global sediment chemoautotrophy would then total 0.15 Pg C y^{-1}. *Thomsen and Kristensen* [1997] measured chemoautotrophic consumption of inorganic carbon in sandy sediments and found that inorganic carbon fixation accounted for 8–10% of sediment respiration. *Howarth* [1984] estimated that chemoautotrophy consumed 10 to 18% of the heterotrophic carbon dioxide production in high activity sediments, but only 3 to 6% in low activity coastal sediments. These numbers are more in line with our lower, conservative estimate of 0.15 Pg C y^{-1}.

[9] A summary of inorganic carbon fixation rates per oceanic environments is presented in Table 1. Chemoautotrophy in sediments (0.37 Pg C y^{-1}) is of similar size to that in the water column: 0.29 Pg C y^{-1} in the euphotic zone and 0.11 Pg C y^{-1} in the dark ocean. However, most sediment chemoautotrophy occurs in coastal and ocean margin sediments and can be attributed to microbes oxidizing reduced iron, manganese and in particular sulfide, whereas water-column chemoautotrophy is due to nitrification and occurs mainly in the open ocean. Overall near-shore, shelf, slope and open ocean settings account for 25, 17.5, 13.9 and 43.6%. This partitioning between oceanic environments as well as absolute rates of chemoautotrophy depend on some of our basic assumptions. Our estimates are based on the global carbon cycling synthesis of *Dunne et al.* [2007] and would inherit any bias in that study. Their primary production and export production/dark ocean respiration rates are fully consistent with most recent carbon budgets [*Dunne et al.*, 2007], indicating that our water-column rates are consistent with published balanced carbon budgets.

Table 1. Organic Carbon Fluxes in the Ocean (Pg C y^{-1})[a]

	Near-Shore	Shelf	Slope	Open	Total
Area (10^{13} m^2)[b]	0.71	0.95	2.24	31.07	34.97
Net Primary Production Phototrophs[b]	3.61	2.87	4.06	43.1	53.6
Euphotic Zone Respiration[b]	2.47	2.01	3.06	36.0	44.0
Dark Ocean Respiration[b]	0.04	0.34	0.64	6.24	7.26
Sediment Respiration[b]	0.53	0.29	0.22	0.19	1.23
Euphotic Zone Chemoautotrophy	0.016	0.013	0.020	0.237	0.286
Dark Ocean Chemoautotrophy	0.002	0.006	0.010	0.096	0.114
Sediment Chemoautotrophy	0.175	0.116	0.077	0.004	0.372

[a]Details of the calculations are provided in the auxiliary material.
[b]Oceanic depth regimes, their surface area (m^2) and estimates for net primary production, respiration in the euphotic zone, the dark ocean and sediment are from *Dunne et al.* [2007].

Sediment organic carbon mineralization rates of *Dunne et al.* [2007] (1.23 Pg C y^{-1}) are somewhat higher than another global carbon budget (0.93 Pg C y^{-1} [*Muller-Karger et al.*, 2005]), which would then lead to overestimates of sediment chemoautotrophy. However, their sediment carbon respiration numbers are lower than data based estimates (2.6 Pg C y^{-1} [*Smith and Hollibaugh*, 1993]; 1.8 Pg C y^{-1} [*Middelburg et al.*, 1997]; 1.5 Pg C y^{-1} [*Glud*, 2008]), implying that an underestimation is more likely.

[10] Our global estimate of chemoautotrophy is based on chemical energy released upon mineralization of organic matter. Other sources of reduced chemical inorganic compounds such a sulfide, hydrogen and reduced iron from hydrothermal vents and water-rock interactions also support chemosynthetic food webs [*Edwards et al.*, 2005; *German et al.*, 2011]. However, there are very few data on their global significance. Oxidation of sulfides in hydrothermal vents has been estimated to support a dissolved inorganic carbon fixation rate of 0.002 Pg C y^{-1} [*Raven*, 2009]. Iron, sulfide and hydrogen in basaltic ocean crust support a carbon fixation rate of 0.001 Pg C y^{-1} [*Bach and Edwards*, 2003]. These two systems combined are of similar magnitude as nitrifier supported chemoautotrophy in deep-sea sediments (0.004 Pg C y^{-1}; Table 1), suggesting that chemoautotrophy driven by organic matter recycling is globally two orders of magnitude more important than that due to water-rock interaction.

[11] Organic matter fluxes into the ocean drive biogeochemical cycles and fuel marine foodwebs. Knowledge of organic matter input rates is therefore of the utmost importance. Although carbon fixation by chemoautotrophs (0.37 to 0.77 Pg C y^{-1} for lower and best estimate, respectively) is only a small fraction of that linked to oceanic photosynthesis (48 to 54 Pg C y^{-1}) [*Field et al.*, 1998; *Dunne et al.*, 2007], it is similar to that of riverine organic carbon delivery (0.4–0.5 Pg C y^{-1} [*Cole et al.*, 2007]) and organic carbon burial in marine sediments (0.2–0.79 Pg C y^{-1} [*Duarte et al.*, 2005; *Burdige*, 2007; *Dunne et al.*, 2007]). This implies that chemoautotrophy should be explicitly included in oceanic carbon budgets and cycling models. Although, carbon fixation by chemoautotrophs represents input of new organic carbon to the ocean, it should be considered secondary rather than primary production because the energy came originally from organic matter.

[12] Chemoautotrophy results in production of new, labile organic carbon in environments otherwise dominated by refractory organic carbon. This local production can dominate carbon input at redox interfaces in the sediments or water column [*Taylor et al.*, 2001], and to marine animals via symbioses [*Dubilier et al.*, 2008]. This significance of chemoautotrophy is not limited to distinct redox interfaces because natural radiocarbon isotope signatures of microorganisms in the mesopelagic ocean revealed significant chemoautotrophic support of microbial communities [*Hansman et al.*, 2009]. Consistently, carbon demand studies of microbes in the dark ocean imply that substantial chemoautotrophic carbon inputs are required to sustain communities [*Arístegui et al.*, 2009; *Baltar et al.*, 2010]. The implications of chemoautotrophy for marine food-web functioning and ocean biogeochemical cycles remain to be investigated: we have to identify the organisms involved, to assess the consequences for oxygen, carbon and nitrogen stoichiometry and to elucidate the fate of chemoautotrophic production.

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