Final Report

Brilliant Marine Research Idea 2024

1. General information

Title of the idea	Small animals with a big impact: how bioturbators counteract climate change
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2. Brilliant Marine Research Idea – Report about the activities

Abstract

Coastal and shelf sediments account for approximately 40% of the global oceanic alkalinity input, making them crucial for the sequestration of CO_2. Globally, the dissolution of calcium carbonate ($CaCO_3$) and the precipitation and burial of pyrite (FeS_2) are the main processes producing net alkalinity in marine sediments, yet they occur in geochemically distinct environments. Dissolution of $CaCO_3$ occurs in the oxygenated, surficial part of the sediment, where the oxidation of reduced compounds and oxic respiration by animals and microbes lower the pH and increase dissolution rates. In contrast, the precipitation of FeS_2 in the deeper, anoxic layers of the sediment also generates alkalinity. However, both $CaCO_3$ dissolution and FeS_2 precipitation are influenced by bioturbation, the mixing and flushing of sediments by animals. Bioturbation can enhance the $CaCO_3$ dissolution by increasing the O_2 availability in the sediment. Simultaneously, introducing O_2 to anoxic sediment layers can cause the reoxidation of FeS_2, leading to the consumption of the alkalinity generated during its formation. The overall impact of bioturbation on net alkalinity production through these opposing mechanisms, however, remains unclear.

Here, we investigated the interactions between natural alkalinity-generating processes in sediments with and without bioturbation. To quantify the relative importance of these processes in different conditions, we studied salt marsh ponds in Blakeney (Norfolk, UK), where bioturbated and unbioturbated ponds are naturally present just a few meters apart. We conducted in-situ sediment-water flux measurements, detailed investigations of the sediment geochemistry and measurements of bioturbation to explore the interactions between geochemical processes and quantify the net effect of bioturbation on alkalinity production. Bioturbation substantially decreased the burial of FeS_2 and generally displayed high alkalinity effluxes, likely due to $CaCO_3$ dissolution. In addition to bioturbation, the coverage of O_2-producing benthic microalgae and the production rate of reduced

compounds in the anoxic sediment further influenced the alkalinity release. Hence, shifts in benthic fauna communities can significantly affect the alkalinity generation in coastal sediments and should be accounted for when assessing the impacts of changes to coastal systems.

Intro

The ocean stores 40 times more carbon dioxide (CO_2) than the atmosphere.[1] This CO_2 storage capacity is regulated by the seawater's alkalinity content, defined as the excess of proton acceptors (bases) over proton donors (acids).[1] A higher oceanic alkalinity content increases the solubility of CO_2 in seawater, and this process controls atmospheric CO_2 concentrations and Earth's climate on a timescale of hundreds to thousands of years.[2] Due to the urgent need to remove CO_2 from the atmosphere, there is considerable interest in processes that change the alkalinity content of the ocean.

Chemical processes in coastal and shelf sediments contribute 25% of the alkalinity input to the ocean[3]. Most sedimentary alkalinity production globally (~50%) stem from calcium carbonate ($CaCO_3$) dissolution[4,5], which occurs in the oxygenated surficial part of the sediment, where oxic respiration by animals and microbes lowers the pH and increases the dissolution rate.[6–8] In the deeper, anoxic part of the sediment, alkalinity is formed through precipitation of pyrite (FeS_2), which contributes ~25% to the global sedimentary alkalinity release.[4,9] FeS_2 is unreactive in anoxic environments and is, if undisturbed, eventually buried by downward advection. If exposed to oxygen (O_2), however, FeS_2 can be reoxidized[10] and the alkalinity generated through its formation is consumed.

Biogeochemical processes in sediments are intimately linked, and changes in the rate of one process often result in concomitant changes to other processes.[3,11] However, interactions in the alkalinity cycle and resulting net effect on the alkalinity production are poorly understood.[12–14] One example of a process that affects the interactions between alkalinity-generating processes in sediments is bioturbation, the mixing (biomixing) and flushing (bioirrigation) of the sediment by animals. Bioturbation has been suggested to enhance the $CaCO_3$ dissolution by increasing the O_2 availability in the sediment.[8,15,16] Simultaneously, the introduction of O_2 to anoxic sediment layers can cause reoxidation of FeS_2.[17] While it is known that bioturbation can affect the sedimentary alkalinity production, the mechanisms are unclear.

It is difficult to isolate the effect of bioturbation on geochemical processes since the vast majority of the modern seafloor is inhabited by animals. Unbioturbated control sites with equivalent geochemical baseline conditions are rare, but crucial to truly elucidate the effect of bioturbation on alkalinity-generating processes. Commonly, geochemical effects of bioturbation are measured in laboratory incubations, as they allow the controlled manipulation of the sediment. However, these incubations are often done in sediments that have previously been defaunated, which impacts the sediment chemistry.[18] Furthermore, bioturbators are known to change their behaviour in incubation conditions[19,20].

However, a salt marsh in Blakeney (United Kingdom) offers a unique opportunity to study the impact of bioturbation on sediment geochemistry. The area consists of several ponds within the same geochemical environment, yet some host bioturbating organisms while others do not. This distribution

of bioturbators have given rise to distinct geochemical conditions in the two types of ponds.[21,22] The Blakeney salt march system has previously been used to investigate the effects of bioturbation on the sedimentary cycles of phosphorus, iron and sulphur.[21–25] In this study, we conducted sediment-water flux measurements, bioirrigation and biomixing measurements, and geochemical characterisation of the porewater and sediment in ponds with and without animals in the Blakeney salt march system, to determine the effect of bioturbation on the sedimentary alkalinity production.

Material & Methods

Field sampling

The Blakeney salt marsh area was visited the 10th – 17th of October 2024. Six ponds were studied; a more extensive sampling was conducted in ponds A (bioturbated) and F (unbioturbated), while a basic sampling was conducted in ponds B (low bioturbation), C (bioturbated), D (unbioturbated), and E (bioturbated). The ponds were 1-2 m in diameter and ca 30 cm deep. The sampling aimed to estimate $CaCO_3$ dissolution rates (^{13}C-DIC and Ca/Mg fluxes, ^{13}C-DIC and Ca/Mg in the porewater, solid phase inorganic carbon), FeS_2 burial rates (Fe and S in the pore water, solid phase FeS_2, sediment accumulation rates), and their respective contribution to the sedimentary alkalinity release (alkalinity flux). We also measured bioirrigation (uranine incubation) and biomixing (radioisotopes).

Sediment-water fluxes and bioirrigation

Sediment-water fluxes of dissolved compounds were measured *in situ* through chamber incubations. Three plexiglass chambers (diameter 19 cm), connected to a portable battery (Instagrid One Max), were inserted directly into the pond. A central stirring disk in the chamber was gently rotated to keep the overlying water well-mixed. Incubations went on for ~6 hours. Oxygen sensors (OXROB10, Pyroscience) continuously measured the oxygen concentrations within the chambers. Discrete water samples were collected at 1-2 hours intervals. In ponds A and F, samples were collected for alkalinity, DIC, d^{13}C-DIC, and Ca/Mg (OES) analysis. In ponds B-E, samples were collected for alkalinity and DIC. In parallel with the flux measurements, bioirrigation rates were estimated using the fluorescent tracer uranine. Two sensors (Cyclops-7F, Turner Designs) were mounted in each pond before addition of uranine which was gently mixed throughout the water. The uranine measurements were conducted over a period of ~6 hours. During the incubations, the ponds were covered with tarpaulins to avoid photosynthesis in the incubation chambers and degradation of the uranine. Bioirrigation rates were calculated from the change in uranine concentration over time using a one-dimensional mechanistic model[26].

Sediment geochemistry

Sediment cores were collected for geochemical characterization of the pore water and solid phase. From ponds A and F, duplicate cores were sliced in air for measurement of alkalinity and DICin the pore water, and inorganic carbon (including ^{13}C) in the solid phase. A second set of duplicate cores were sliced in a glove bag under nitrogen gas atmosphere for measurement of hydrogen sulphide (H_2S), Ca/Mg/Fe/S (OES), and d^{13}C-DIC in the porewater, and S and Fe contents in the solid phase. The porewater was extracted using Rhizons. Additional cores were collected for calculation of sediment porosity and subsequent measurements of radioisotopes (^{210}Pb, ^{137}Cs and ^{7}Be), which

were used to estimate biomixing and sediment accumulation rates, and for measurements of porewater methane (CH_4) concentrations. From ponds B-E, one core was collected for measurement of alkalinity and DIC in the pore water as well as inorganic carbon in the solid phase, and a second core was used to measure the porosity. Microsensor measurements of O_2, H_2S and pH were conducted on cores from all ponds and sediment was sieved for collection of benthic animals.

Further analyses
A delay in the installation of an oven for drying sediment samples has in turn delayed the analysis of the solid phase geochemistry. These analyses are currently ongoing and results are expected imminently. Once the solid phase composition is available, the data will be analysed with a biogeochemical model (Virtual seafloor[27,28]).

Results/Conclusions

Impact of bioturbation on the sediment geochemistry
Burrowing worms were prevalent in the bioturbated ponds (A, C, E), and a few small worms were also found in pond B, which had originally been identified as unbioturbated. No bioturbating animals were found in ponds D and F. Radioisotope data suggested biomixing to ~10 cm depth in the bioturbated ponds, whereas no mixing was detected in the unbioturbated ponds. The uranine measurements showed distinctly different bioirrigation regimes in the bioturbated and unbioturbated ponds.

Clear geochemical differences were observed between bioturbated and unbioturbated ponds. Due to the mixing and irrigation by animals, the porewater profiles in the bioturbated ponds changed little over the top 10 cm and concentrations of solutes were similar to the overlying water. Bioturbation caused a considerable deepening of the O_2 penetration depth and no H_2S or CH_4 were detected in the bioturbated ponds. In the unbioturbated ponds, alkalinity and DIC accumulated with depth in the porewater, in accordance with production throughout the sediment and diffusion to the water. The O_2 penetration was lower than in the bioturbated ponds, H_2S was present nearly until the sediment surface and CH_4 was detected in the porewater. The low-bioturbation pond B showed characteristics in-between the fully bioturbated (A, C, E) and unbioturbated (D, F) ponds.

Dynamics of $CaCO_3$ and FeS_2 and the resulting alkalinity release
In general, alkalinity was released from the sediment in bioturbated ponds and taken up in unbioturbated ponds. However, the differences between replicate incubation chambers in the same pond were sometimes substantial, showing opposing directions in the flux. Data on $d^{13}C$-DIC and Ca fluxes similarly indicated strong local variations in the $CaCO_3$ dissolution, correlating with the alkalinity release rates.

In the bioturbated ponds, the deepening of the O_2 penetration depth and resulting increase in oxic organic matter mineralisation caused clear subsurface pH minimums (7 – 7.5). The pH remained relatively low throughout the sediment and the porewater was undersaturated with regards to $CaCO_3$, indicating that dissolution was occurring and producing alkalinity. Interestingly, in the unbioturbated ponds, the high availability of H_2S and O_2 close to the sediment surface led to intense reoxidation of H_2S, which caused an even stronger decrease in the sedimentary pH (6.5 – 7). Below the surface sediment, the pH increased substantially and the porewater was oversaturated with regards to

$CaCO_3$. Porewater profiles of Ca suggest that some $CaCO_3$ precipitation may have occurred in the deeper sediment, which would have consumed alkalinity. However, in pond F, the presence of O_2-producing benthic microalgae at the sediment surface caused a strong local decreases in pH, and porewater profiles and flux data indicated $CaCO_3$ dissolution. Overall, the distribution of low-pH environments at the sediment surface was patchy and linked to the proximity to bioturbators and local abundance of O_2-producing benthic microalgae, in agreement with the variation in alkalinity effluxes within ponds. Importantly, since the activity of benthic microalgae varies over diurnal and seasonal cycles, their role in the sedimentary alkalinity production is likely equally variable.

The high concentration of H_2S and absence of dissolved Fe in the porewater intimated formation of FeS_2 in the unbioturbated sediment. In the bioturbated ponds, the absence of H_2S and detection of dissolved Fe suggested that net formation of FeS_2 was negligeable. While these hypothesis remain to be confirmed by the solid phase analysis, they align with previous measurements of FeS_2 in the area[21,25]. The FeS_2 likely contributed strongly to the production of alkalinity in the sediment, together with anaerobic reoxidation of CH_4 with H_2S. However, the sedimentary uptake of alkalinity in most of the unbioturbated ponds suggested that this sedimentary alkalinity production was outcompeted by the consumption of alkalinity through intense reoxidation of reduced compounds with O_2. As such, the production and consumption of alkalinity in the unbioturbated ponds likely change with time due to seasonal variations in the input of organic matter and resulting build-up of reduced compounds.

Conclusions

The Blakeney salt march area offers an exceptional opportunity to study the impact of bioturbation on sediment geochemistry as it naturally consists of ponds with and without animals. Here, we used this unique feature to investigate the impact of bioturbation on alkalinity-generation in the seafloor. Ponds with and without animals displayed distinct geochemical characteristics. In general, the sedimentary alkalinity generation was higher in the bioturbated ponds, likely as a result of $CaCO_3$ dissolution. Intense reoxidation of reduced compounds and possible precipitation of $CaCO_3$ caused a sedimentary uptake of alkalinity in most of the unbioturbated ponds. However, production of O_2 by benthic microalgae substantial lowered the sediment pH in some parts of one unbioturbated pond, driving a release of alkalinity through localised dissolution of $CaCO_3$. In conclusion, the activity of benthic animals has a strong impact on alkalinity generation in sediments. Hence, shifts in benthic fauna communities can significantly affect the production of alkalinity in coastal sediments and should be accounted for when assessing the impacts of changes to coastal systems.

References

1. Zeebe and Wolf-Gladrow (2001) *CO2 in seawater : equilibrium, kinetics, isotopes*. Elsevier, Amsterdam. **2.** Berner (2004) *The Phanerozoic Carbon Cycle: CO2 and O2*, Oxford University Press, USA. **3.** Krumins et al. (2013) *BG* 10. **4.** Middelburg et al. (2020) *Rev. Geophys.* 58. **5.** Müller et al. (2022) *GBC* 36. **6.** Morse and Mackenzie (1990) *Geochemistry of sedimentary carbonates*. Elsevier. **7.** Milliman and Droxler (1996) *Geologische Rundschau* 85. **8.** Rao et al. (2014) *Estuar. Coast. Shelf Sci.* 148. **9.** Hu and Cai (2011) *GBC* 25. 10. Rimstidt and Vaughan (2003) *GCA* 67. **11.** Wolf-Gladrow et al. (2007) *Mar. Chem.* 106. **12.** Berner et al. (1970) *L&O* 15. **13.** Rassmann et al. (2016) *BG* 13. **14.** Walter et al. (1993) *Phil. Trans. R. Soc. Lond. A* 344. **15.** Aller (1982) *J. Geol.* 90. **16.** Michaud et al. (2021) *J. Mar. Res.* 79. **17.** Schippers and Jørgensen (2002) *GCA* 66. **18.** Stocum and Plante (2006) *J. Exp. Mar. Bio. Ecol.* 337. **19.** Glud et al. (2003) *L&O* 48. **20.** Hammond et al. (2004) *L&O Methods* 2. **21.** van de Velde et al. (2020) *GCA* 276. **22.** van de Velde et al. (2021) *BG* 18. **23.** Mills et al. (2016) *EPSL* 453. **24.** Hutchings et al. (2019) *Front. Earth Sci.* 7. **25.** Antler et al. (2019) *Front. Earth Sci.* 7. **26.** De Borger et al. (2020) *BG* 17. **27.** Soetaert and Meysman (2012) *Environ. Modell. Softw.* 35 **28.** van de Velde et al. (2018) *Sci. Rep.* 8.

3. Overview of the expenditures

- Accommodation in Blakeney during fieldwork. Airbnb hosting five researchers for six nights (10 Oct – 16 Oct 2024): € 954.25

- Rental of rechargeable battery for powering flux incubation chambers, O_2 sensors and uranine sensors in the field (10 Oct – 16 Oct 2024): € 147.59

- Rental of minivan for transport from Antwerp to Blakeney and back (9 Oct – 17 Oct 2024) + car insurance for travelling abroad: € 672.2 (572.73 + 99.47)

- Tickets Eurotunnel return trip (10 Oct & 16 Oct 2024): € 313

- Analysis of samples by inductively coupled plasma optical emission spectroscopy (ICP-OES), 45 porewater samples and 36 flux incubation samples, Utrecht University: € 1901.03

- Analysis of samples by isotope ratio mass spectrometry (IRMS), 34 porewater samples and 36 flux incubation samples, KU Leuven: € 1008

Total sum: € 4996.07

4. Pictures

A set of five pictures (low resolution in this document). The five high resolution pictures should be delivered to VLIZ by email to karen.rappe@vliz.be.
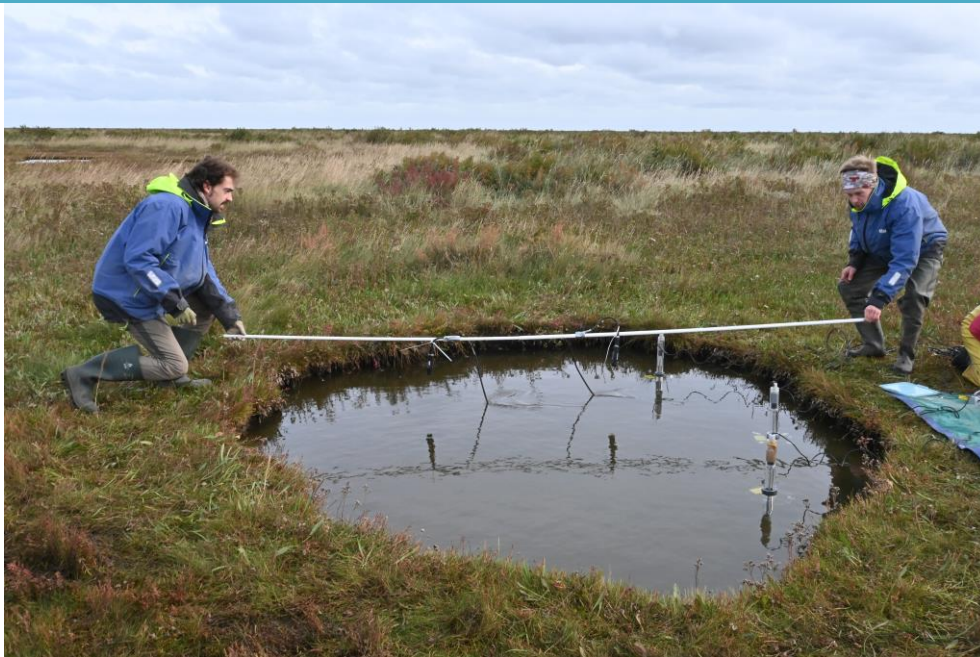
Figure 1 Salt marsh ponds in Blakeney, Norfolk (UK).

Figure 2 Installation of incubation chambers for measuring sediment-water fluxes of dissolved compounds.

Figure 3 Installation of uranine sensors for measuring bioirrigation.

Figure 4 Collection of sediment cores for geochemical analysis.

Figure 5 Worm cast and burrows in a bioturbated pond.