Alkalinity production coupled to pyrite formation represents an unaccounted blue carbon sink

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Abstract

Coastal vegetated habitats, including mangroves, saltmarshes and seagrasses, mitigate climate change by storing atmospheric carbon. Previous blue carbon research has mainly focused on organic carbon stocks. However, recent studies suggest that lateral inorganic carbon export might be equally important. Lateral export is a long-term carbon sink if carbon is exported as alkalinity (TAlk) produced via sulfate reduction coupled to pyrite formation. This study evaluates drivers of pyrite formation in coastal vegetated habitats, compares pyrite production to TAlk outwelling rates, and estimates global pyrite stocks in mangroves. We quantified pyrite stocks in mangroves, saltmarshes and seagrasses along a latitudinal gradient on the Australian East Coast, including a mangrove dieback area, and in the Everglades (Florida, USA). Our results indicate that pyrite stocks were driven by a combination of biomass, tidal amplitude, sediment organic carbon, sedimentation rates, rainfall latitude, temperature, and iron availability. Pyrite stocks were three-times higher in mangroves (103 ± 61 Mg/ha) than in saltmarshes (30 ± 30 Mg/ha) and seagrasses (32 ± 1 Mg/ha). Mangrove pyrite stocks were linearly correlated to TAlk export at sites where sulfate reduction was the dominant TAlk producing process, however pyrite generation could not explain all TAlk production. We present the first global model predicting pyrite stocks in mangroves, which average 155 (range 128 – 182) Mg/ha. In mangroves, estimated global TAlk production coupled to pyrite formation (~3 mol/m²/y) is equal to ~24% of their global organic carbon burial rate, thus highlighting the importance of including TAlk export in future blue carbon budgets.

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Key Points

- Alkalinity export from coastal vegetated habitats is a long-term carbon sink if alkalinity production is coupled to pyrite formation
- We present the first global model for pyrite stocks in mangroves, showing that mangrove pyrite stocks amount to, on average, 155 Mg/ha
- Pyrite formation in mangroves produces between 0.37 and 0.52 Tmol TAlk per year globally, making the process a substantial carbon sink

1 Abstract

2 Coastal vegetated habitats, including mangroves, saltmarshes and seagrasses, mitigate climate change by storing atmospheric carbon. Previous blue carbon research has mainly 3 4 focused on organic carbon stocks. However, recent studies suggest that lateral inorganic 5 carbon export might be equally important. Lateral export is a long-term carbon sink if carbon is exported as alkalinity (TAlk) produced via sulfate reduction coupled to pyrite formation. 6 7 This study evaluates drivers of pyrite formation in coastal vegetated habitats, compares pyrite 8 production to TAlk outwelling rates, and estimates global pyrite stocks in mangroves. We 9 quantified pyrite stocks in mangroves, saltmarshes and seagrasses along a latitudinal gradient 10 on the Australian East Coast, including a mangrove dieback area, and in the Everglades 11 (Florida, USA). Our results indicate that pyrite stocks were driven by a combination of 12 biomass, tidal amplitude, sediment organic carbon, sedimentation rates, rainfall latitude, 13 temperature, and iron availability. Pyrite stocks were three-times higher in mangroves (103 \pm 14 61 Mg/ha) than in saltmarshes (30 \pm 30 Mg/ha) and seagrasses (32 \pm 1 Mg/ha). Mangrove 15 pyrite stocks were linearly correlated to TAlk export at sites where sulfate reduction was the 16 dominant TAlk producing process, however pyrite generation could not explain all TAlk 17 production. We present the first global model predicting pyrite stocks in mangroves, which 18 average 155 (range 128 - 182) Mg/ha. In mangroves, estimated global TAlk production 19 coupled to pyrite formation (~3 mol/m²/y) is equal to ~24% of their global organic carbon 20 burial rate, thus highlighting the importance of including TAlk export in future blue carbon 21 budgets.

22 Plain Language Summary

23 Coastal vegetated habitats (i.e., mangroves, saltmarshes and seagrasses) buffer 24 climate change by capturing carbon dioxide. The potential of these habitats to offset 25 anthropogenic climate change is currently evaluated by measuring the amount of carbon that 26 accumulates in coastal vegetated sediments. However, sedimentary carbon may be partly 27 decomposed by microorganisms and can be exported to the coastal ocean. Exported carbon 28 can be a permanent carbon sink if the carbon decomposition is coupled to the formation of 29 iron sulfide minerals. This study explores the drivers and global relevance of iron sulfide 30 mineral formation and the associated carbon export in coastal vegetated habitats. We found 31 that biological, climatic and geological factors, can predict iron sulfide mineral formation. 32 Based on these relationships, we developed the first global model predicting iron sulfide 33 mineral stocks in mangroves and found that the associated dissolved carbon generated was 34 equal to a quarter of the carbon stored in mangrove sediments. This highlights the importance 35 of considering dissolved carbon export when evaluating the potential of coastal vegetated 36 habitats to buffer climate change.

37 Keywords

- 38 Coastal carbon cycling
- 39 Mangrove carbon budget
- 40 Alkalinity generation
- 41 Sulfur cycling
- 42 Iron sulfide minerals
- 43 Chromium reducible sulfur

44 **1 Introduction**

Coastal vegetated habitats, such as mangroves, saltmarshes and seagrasses, mitigate 45 climate change by sequestering and storing atmospheric carbon. Carbon sequestration and 46 47 storage per unit area is considerably higher in coastal vegetated habitats compared to terrestrial ecosystems (Mcleod et al., 2011; Nellemann & Corcoran, 2009) and has been 48 49 referred to "blue carbon". Previous blue carbon research focused mainly on sedimentary and 50 biomass carbon stocks to evaluate the capacity of coastal vegetated habitats to mitigate climate change (Brown et al., 2016; Donato et al., 2011; Fourgurean et al., 2012; Kauffman 51 52 & Bhomia, 2017; Kelleway et al., 2016). However, in addition to carbon stocks, dissolved 53 carbon export is a significant, but so far largely unaccounted, blue carbon sink (Ho et al., 54 2017; Maher et al., 2018; Maher et al., 2013; Santos et al., 2019).

55 Dissolved carbon export from coastal vegetated habitats can be considered a long-56 term carbon sink if carbon is exported as alkalinity (TAlk), since exported TAlk has a residence time in the ocean of ~ 1×10^5 years (Emerson & Hedges, 2008; Middelburg et al., 57 58 2019). Flushing of porewater TAlk followed by lateral export to the coastal ocean is a major 59 carbon sink in mangroves and saltmarshes (Sippo et al., 2016; Wang & Cai, 2004). 60 Sedimentary processes that couple organic matter degradation and TAlk production include 61 denitrification, manganese reduction, iron reduction and sulfate reduction (Burdige, 2011; 62 Krumins et al., 2013). However, oxidation of reduced compounds (e.g. sulfide) may consume 63 neo-formed TAlk prior to being exported. Therefore, only a permanent spatial decoupling of 64 anaerobic remineralisation products from TAlk, such as loss via nitrogen gas from 65 denitrification and precipitation of reduced sulfur as sedimentary pyrite, can contribute to net 66 TAlk production (Hu & Cai, 2011). Due to nitrogen limitation, denitrification rates in pristine 67 coastal vegetated habitats are usually low (Bianchi, 2007), and as such sulfate reduction 68 coupled to pyrite formation is often the dominant net TAlk production process coupled to 69 organic matter degradation in pristine coastal vegetated habitats.

70 In coastal sediments, pyrite (FeS₂) is formed via several, complex pathways. A 71 common pathway involves iron(II) sulfide (FeS) as an initial precursor, which is formed from the reaction of sulfide, produced by microbially mediated sulfate reduction, with ferrous iron 72 73 (Fe²⁺) or with reactive iron(III) oxides (Schoonen & Barnes, 1991). Since sulfur in pyrite is 74 slightly more oxidised (S-I) than in sulfide (S-II), pyrite is produced via intermediate redox 75 reactions, including partial oxidation of FeS. Pyrite formation mainly occurs in upper 76 sediment layers, where reactive iron concentrations and sulfate reduction rates are sufficiently 77 high due to mixed redox conditions, adequate sulphate supply from surface waters, and 78 available labile organic matter (Burdige, 2011; Wada & Seisuwan, 1986). Within this 79 biogeochemically dynamic layer, pyrite can form via reaction of FeS with polysulfide (S_2^{x-}) 80 or via a greigite intermediary (Fe₃S₄) (Goldhaber, 2003; Rickard & Luther, 2007). 81 Alternatively, FeS can react with hydrogen sulfide to form pyrite and hydrogen gas (Rickard, 82 1997), especially within deeper sediment depths where sulfide concentrations are often 83 comparatively high. Howarth (1979) observed that in saltmarshes, pyrite can also form 84 rapidly without FeS as an initial precursor. In situ rates of pyrite formation depend on a wide 85 range of environmental conditions (Burton et al., 2011).

The availability of sulfate, organic carbon and reactive iron are key factors controlling pyrite formation in coastal sediments (Berner, 1970, 1984). In coastal vegetated habitats, tidal seawater inundation resupplies the sulfate required for sulfate reduction. Therefore, sulfate is usually only limiting in upper estuarine freshwater reaches (where the salinity drops below 2.5 - 4), where sediments are impermeable, or in extremely carbon rich sediments (Burdige, 2011). Sulfate reduction also requires a source of organic carbon. Even though coastal

92 vegetated habitats are generally carbon rich, their carbon content is variable and depends on 93 climatic factors, geomorphology, hydrology, vegetation species composition, nutrient 94 availability and sedimentation rates (Kristensen et al., 2008; Macreadie et al., 2014; Ouyang 95 & Lee, 2014; Sasmito et al., 2020). In carbon rich systems (>15% sediment organic carbon content), reactive iron availability can also limit pyrite formation (Berner & Raiswell, 1984). 96 97 The availability of reactive iron depends on regional geology, sediment texture, weathering and sedimentation rates (Kendall et al., 2012; Raiswell & Canfield, 2012). Whether sulfate, 98 99 organic carbon or reactive iron limits pyrite formation is highly site specific (Morse et al., 100 2007), hence modelling these processes is a challenge.

101 This study aims to evaluate alkalinity production coupled to pyrite formation in 102 coastal vegetated habitats and to examine whether pyrite stocks represent a significant blue 103 carbon sink. To achieve this, we quantified pyrite stocks in mangroves, saltmarshes and seagrasses along a latitudinal gradient. We also investigated relationships between pyrite 104 105 stocks and key underlying drivers to develop a global model for mangrove pyrite stocks in 106 order to provide a basis for estimating the pyrite-associated global mangrove TAlk generation. In order to investigate small-scale variability in pyrite stocks and consequences of 107 108 vegetation disturbance on pyrite stocks, we conducted two case studies - one within a large, pristine mangrove system in Florida, USA and a second in a mangrove dieback area in 109 Australia. We tested whether pyrite stocks can be used as a proxy for TAlk generation / 110 111 export locally and hypothesise that pyrite stocks provide an important indirect means for 112 estimating what is currently an uncounted blue carbon sink.

113 2 Methods

114 2.1 Study sites

We investigated pyrite stocks in three areas that span the general range of climatic, biomass, diversity, and sediment carbon stocks observed in mangroves globally, as well as covering a range in catchment geology (Figure 1, Table 1). Firstly, at Everglades National Park in Florida, USA, which contains the largest continuous mangrove forest in North America (144,447 ha), sampling was conducted along the Shark River estuary. The Shark River estuary is dominated by mangroves, with a transition to freshwater marsh areas in the freshwater reaches.

Secondly, we sampled an Australian mangrove dieback area located in the Gulf of Carpentaria near Karumba. During late 2015 and mid 2016 more than 7,400 ha of mangrove forest died as a result of high temperatures, drought and a rapid drop in sea levels during the pre-monsoon dry season (Duke et al., 2017; Lovelock et al., 2017). The Norman River separates a dead mangrove stand from an adjacent living mangrove area, allowing direct comparison to test the effect of the mangrove dieback on pyrite stocks in an identical climate zone.

Thirdly, we conducted sampling along a latitudinal gradient at the Australian East Coast (Figure 1, Table 1). Sampling areas along the latitudinal gradient from 12° to 38° included mangroves, saltmarshes and seagrasses located in Darwin, Hinchinbrook Island, Rockhampton, Seventeen Seventy, River Heads, Sunshine Coast, Jacobs Well, Ballina, Coffs Harbour, Queens Lake, Newcastle, Sydney and Barwon Heads.





Figure 1. Study sites (a) along a latitudinal gradient at the Australian East Coast, (b) at the mangrove dieback
 area near Karumba and (c) along the Shark River estuary at the Everglades National Park, Florida, USA.

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Table 1. Location, sampling dates and climate of all study sites. Annual temperature and rainfall were averaged
 between 1982 and 2012 (Climate-Data.org, 2020).

Site	GPS	Sample date (mm/yy)	Climate	Average annual temperature (°C)	Average annual rainfall (mm)
Everglades	25.36247°N. 81.0847°W	11/19	Subtropical	23.6	1534
Darwin	12.51966°S, 130.90603°E	08/14	Tropical	27.4	1694
Karumba	17.39480°S, 140.87355°E	08/18	Tropical	27.1	876
Hinchinbrook Island	18.24400°S, 146.22800°E	07/14	Tropical	24.2	2001
Rockhampton	23.50949°S, 150.78940°E	02/19	Subtropical	22.3	890
Seventeen Seventy	24.19202°S, 151.56975°E	07/14, 2/19	Subtropical	22.1	1196
River Heads	25.40981°S, 152.89394°E	02/19	Subtropical	21.6	1225
Sunshine Coast	26.61198°S, 153.05518°E	02/19	Subtropical	20.5	1788
Jacobs Well	27.78094°S, 153.37962°E	11/13, 2/19	Subtropical	19.9	1555
Ballina	28.82454°S, 153.57198°E	01/19	Subtropical	19.7	1805
Coffs Harbour	30.29447°S, 153.11755°E	04/20	Subtropical	18.8	1688
Queens Lake	31.63441°S, 152.79648°E	01/19	Subtropical	17.9	1579
Newcastle	32.85146°S, 151.76753°E	11/14, 1/19	Subtropical	18.0	1139
Sydney	34.00988°S, 151.19168°E	02/19	Subtropical	17.6	1309
Barwon Heads	38.25716°S, 144.48700°E	11/14	Temperate	14.8	666

140 2.2 Sample collection

At Everglades National Park in Florida, USA, two to three sediment cores were taken 141 142 at four sites, between the estuary mouth and the freshwater reaches of the Shark River 143 estuary. At each site, a core was collected adjacent to the river, ~5 m landward from the river, 144 and ~10 m landward from the river. At Karumba, nine sediment cores were taken from the 145 living and nine sediment cores were taken from the dead mangrove area, with triplicate cores taken in the lower, middle and upper stands (~75 m distance). At the sites along the 146 Australian latitudinal gradient, one to three sediment cores were collected per ecosystem: 24 147 148 at mangrove, eleven at saltmarsh and four at seagrass sites. In mangrove and saltmarsh areas, sediment cores were taken from locations close to the low tide mark and at higher intertidal 149 150 areas. In total 66 cores were collected from which 900 depth increments were analysed for 151 pyrite. The maximum sampling depth varied between 33 cm and two meters, with most sediment cores (73%) having a depth of at least 90 cm. 152

153 Sediment cores were extracted with a Russian Peat auger or a gouge auger. The redox 154 potential of the sediment profiles was measured with a handheld digital meter (Hach 40Qd). Samples for acid-volatile sulfide (AVS) and chromium-reducible sulfur (CRS) analysis, 155 156 together known as reduced inorganic sulfur (RIS), were either subsampled on site into plastic 157 bags with all air-removed, and kept frozen or subsampled from sediment cores, which were sealed with plastic shrink wrap, stored frozen and transported to the laboratory. Additional 158 159 sediment samples were taken for dry bulk density, reactive iron and organic carbon 160 measurements. At Darwin, Hinchinbrook Island, Seventeen Seventy, Jacobs Well, Newcastle, 161 and Barwon Heads subsamples were taken to analyse sediment accumulation rates (SAR).

162 At selected Everglades and Karumba sites, porewater profiles were analysed for 163 TAlk, Fe^{2+} , total aqueous iron (Fe^{Tot}) and aqueous sulfide (S(-II)), which includes H₂S, HS⁻ 164 and S²⁻. Porewater extraction was conducted as described by Johnston et al. (2016). Briefly, 165 sediment cores were collected in PVC cores and 10 cm long rhizon samplers were inserted 166 into the cores at increasing depths. Porewater was extracted under vacuum via tubing and 167 Luer-Lock connectors through a needle into N₂ filled, O₂-free 10 ml glass vials, which were 168 sealed with rubber septa. Porewater samples were analysed on the day of collection.

At Karumba, groundwater was sampled for TAlk analysis 1 m adjacent to the sediment core collection site. Boreholes were dug with a post-hole digger and purged three times with a peristaltic pump. Groundwater was allowed to completely recharge prior to sampling. Groundwater TAlk samples were stored cool and measured within one day.

173 2.3 Sample analysis

174 Sediment AVS, which includes intermediaries such as FeS and greigite, was analysed 175 by the diffusion method outlined by Burton et al. (2009), extracting AVS with hydrochloric 176 acid/ascorbic acid and trapping H_2S in an alkaline zinc solution. CRS was quantified 177 sequentially after AVS analysis, using the method developed by Burton et al. (2008). Both 178 AVS and CRS concentrations were determined via iodometric titration of the zinc traps, with 179 a measurement error of 11% (based on repeat duplicate analysis) and a detection limit of 2 180 μ mol/g.

Sediment organic carbon was analysed, as described by Radabaugh et al. (2018). In 181 182 brief, the bulk density was determined by mass loss, drying the samples at 105 °C. 183 Subsequently, organic carbon was determined by the loss-on-ignition (LOI) method, combusting samples at 550 °C. To convert LOI (%) into sediment organic carbon (%) an 184 ecosystem specific conversation factor was used for mangroves (0.42), saltmarshes (0.50) and 185 seagrasses (0.40) (Fourgurean et al., 2012; Radabaugh et al., 2018). In addition, for sediment 186 187 cores taken in Darwin, Hinchinbrook Island, Seventeen Seventy, Jacob's Well, Newcastle and 188 Barwon Heads, organic carbon was analysed using a Flash Elemental Analyzer coupled to a 189 Thermo Fisher Delta V isotope ratio mass spectrometer.

Reactive iron was estimated using the citrate-dithionite extraction method, which
extracts the most reactive iron(III) oxide phases and represents a pool of readily "available"
Fe that can contribute to pyrite formation (Raiswell et al., 1994; Raiswell & Canfield, 2012).
After filtration (0.45 μm), reactive iron was measured by spectrophotometry using the 1,10phenanthroline method (APHA, 2005).

195 Porewater Fe^{2+} , Fe^{Tot} and S(-II) were also measured by spectrophotometry. The 1,10-196 phenanthroline method was used to determine porewater Fe^{2+} and, after reducing Fe^{3+} by 197 adding hydroxylamine, Fe^{Tot} (APHA, 2005). Aqueous S(-II) was analysed using the 198 methylene blue method (Cline, 1969).

199 Groundwater TAlk was determined by a Gran titration using a titrator (Metrohm 888 200 Titrando with Tiamo light) with a precision better than 5 μ M. Drifts and deviations in the 201 acid concentration were corrected using certified reference materials (CRM batch 175 and 202 CRM batch 178), as described by Dickson (2010).

203 SAR was determined examining the nuclear fallout signature of plutonium-239 + 240 204 as described by Sanders et al. (2016b) with an uncertainty of 16%. In brief, samples were 205 dry-ashed, spiked with Pu-242 and filtered (0.45 μ m). To allow conversion from Pu to Pu(IV) samples were standing open for 16 hours. Analysis was performed using a Thermo X2 Seriesquadrupole ICPMS system.

208 2.4 Calculations and statistics

209 Pyrite concentrations were calculated by dividing CRS concentrations by two, 210 assuming that the stoichiometry of pyrite is FeS_2 and that elemental sulfur, which may contribute to CRS, is negligible. These assumptions are reasonable since elemental sulfur is 211 often negligible in coastal vegetated habitats and thus FeS₂ is the dominant form of CRS 212 213 (Ding et al., 2014; Holmer et al., 2006; Johnston et al., 2016). Pyrite and carbon stocks were 214 calculated by summing the pyrite and sediment organic carbon density (concentrations 215 multiplied by the dry bulk density) over the first meter of each sediment core. If cores were 216 shorter than 1 m, the deepest measured pyrite concentration and bulk densities were extrapolated to 1 m. 217

The degree of pyritisation (DOP), a proxy for iron limitation, was calculated according to Berner (1970):

220 DOP = pyrite iron / (pyrite iron + reactive iron), where pyrite iron =
$$0.5 \times CRS$$
 (1)

221 At sites where SAR was determined, TAlk production rates coupled to pyrite 222 formation, as well as carbon burial rates were estimated. Mass accumulation rates (MAR) were calculated as the product of SAR and dry bulk density. Multiplying MAR with the 223 224 carbon concentration at each depth, carbon accumulation rates were calculated and averaged 225 per core. Similarly, pyrite accumulation rates were calculated by multiplying pyrite 226 concentrations with MAR per depth and averaged per core. The TAlk production during pyrite formation is coupled to the stoichiometry of sulfate reduction. During sulfate 227 228 reduction, approximately 2 - 3 TAlk equivalents are produced per mol of reduced sulfate 229 (SO_4^{2-}) , with the ratio depending on the organic substrate, i.e., acetate (CH₃COO⁻), lactate (3CH₃CHOHCOO⁻) or propionate (CH₃CH₂COO⁻) (Sheoran et al., 2010): 230

231
$$CH_3COO^- + SO_4^{2-} + H^+ \rightarrow H_2S + 2HCO_3^-$$
 (2)

232
$$2/3CH_3CHOHCOO^- + SO_4^{2-} + 2/3H^+ \rightarrow H_2S + 2HCO_3^-$$
 (3)

233
$$4/7CH_3CH_2COO^- + SO_4^{2-} + 6/7H^+ \rightarrow H_2S + 12/7HCO_3^-$$
 (4)

Given that 2 mols of reduced sulfur are required for a single mol of pyrite (Blodau, 2006; Johnston et al., 2012), pyrite accumulation rates were multiplied by a conversion factor of 5 to estimate TAlk production rates coupled to pyrite formation. Uncertainty bands were estimated by propagating the error related to the conversion factor (± 1) as well as the measurement errors of the pyrite ($\pm 11\%$) and SAR ($\pm 16\%$) analysis.

239 Statistical analysis was conducted in R-3.6.2. Probability levels for are indicated as * 240 if p < 0.05, ** if p < 0.01 and *** if p < 0 .001. A log-linear model based on site-specific 241 average annual temperature, average annual precipitation, average tidal amplitude, sediment 242 organic carbon, aboveground biomass, and reactive iron in the catchment was developed to predict mangrove pyrite stocks. Constants were calculated through an iterative least-squares 243 process using Microsoft Excel. The resulting model output was used to estimate global pyrite 244 245 stocks in mangroves. The global model inputs included temperature (Fick & Hijmans, 2017), precipitation (Fick & Hijmans, 2017), average tidal amplitude (Vestbo et al., 2018), sediment 246 247 organic carbon (Sanderman et al., 2018), aboveground biomass (Simard et al., 2019), and 248 reactive iron (Rossel et al., 2016). We conducted Monte Carlo error simulations to calculate

- the 25% and 75% quartile error band of the global pyrite stock average by taking the RMSE of the model and running 1,000,000 simulations.

251 **3 Results**

252 3.1 Everglades National Park

At Everglades National Park, bulk density ranged between 0.09 and 0.94 g/cm³ and AVS was below the detection limit in all samples. Pyrite concentrations $(3.4 - 408 \ \mu mol/g)$ were higher at the polyhaline downstream (E1) and mesohaline midstream (E2, E3) sites compared to the oligohaline upstream site (E4) and generally increased with depth (Figure 2). There was no significant difference in the pyrite concentrations with increasing distance from the river.

259 On average, porewater $Fe^{Tot} (0.62 - 25 \mu M)$ was two-times higher at the upstream site 260 (E4) compared to the mid and downstream sites (E1, E3) and decreased with depth. The share 261 of porewater $Fe^{2+} (0.17 - 6.8 \mu M)$ on Fe^{Tot} increased with depth and was highest at the 262 midstream and downstream sites (up to 100% at E1 and E3). Increasing with depth, 263 porewater TAlk (1345 - 14840 μ mol/kg) was two-times higher at the downstream and 264 midstream sites (E1 and E3) compared to the upstream site (E4).



Figure 2. Sediment profiles of (a) pyrite, (b) porewater iron, and (c) porewater alkalinity concentrations at downstream (E1), midstream (E2, E3), and upstream (E4) sites along the Shark River estuary at Everglades National Park, Florida, USA. At each site, cores were taken at an increasing distance from the river (~5m).

269 3.2 Mangrove dieback near Karumba

270 At the Karumba mangrove site, the bulk density varied between 0.37 and 1.7 g/cm³. Concentrations of AVS ranged from 0 to 5.3 µmol/g and were below the detection limit in the 271 majority of the samples. Pyrite reached higher values $(0 - 217 \mu mol/g)$ at the living (K4 -272 K6) than at the dead mangrove area $(0 - 127 \mu mol/g, K1 - K3)$ (Figure 3). Pyrite 273 274 concentrations decreased with distance from the shore, however, this effect decreased with depth, particularly at the dead area. The redox potential indicated anoxic conditions at close 275 proximity to the ocean (-321 to -109 mV), but partly suboxic conditions at mid (-215 to 12 276 277 mV) and distal (-145 to 231 mV) cores.

278 Decreasing with depth, reactive iron was on average two times lower at the living 279 (0.25%) than at the dead (0.41%) area. The DOP was almost twice as high at the living (0.72) 280 than at the dead (0.43) area. Porewater Fe^{2+} ranged from $1 - 57 \mu$ M. At the living area, Fe^{2+} 281 accounted for an average of 24% of Fe^{Tot} (1.6 – 83 μ M), which showed two distinct peaks at 282 20 and 40 cm. At both areas, porewater S(-II) (0.11 – 8543 μ M) and TAlk (1400 – 52000 283 μ mol/kg) increased simultaneously with depth. At the living area, S(-II) increased abruptly 284 just below the lower Fe^{Tot} peak.



Reactive Fe (%) Aqueous iron (µM) S(-II) (µM) TAIK (µmol/kg)
 Figure 3. Sediment profiles of (a) pyrite, (b) redox potential, (c) reactive iron, (d) porewater iron, (e) porewater
 S(-II) and (f) porewater alkalinity at dead mangrove areas (K1 – 3) and living mangrove areas (K4 – 6) near
 Karumba, Australia. At each site, cores were taken at an increasing distance from the ocean (~75m).

289 On average, pyrite stocks were 20% lower at the dead (range 21 - 74 Mg/ha, mean \pm 290 error 50 ± 15 Mg/ha) compared to the living area (1 - 124 Mg/ha, 63 ± 40 Mg/ha) (Figure 4). 291 Pyrite stocks were positively correlated with groundwater TAlk (ranging from 7400 to 48000 292 μ mol/kg) in the living area, ($R^2 = 0.59^*$), but showed no significant correlation at the dead 293 area.



Figure 4. Comparison of (a) pyrite stocks and (b) correlations between pyrite stocks and groundwater TAlk at the dead (n = 9) and living (n = 9) mangrove areas near Karumba, Australia. Grey areas indicate the 95% confidence intervals of the regressions.

298 3.3 Latitudinal gradient

Along the latitudinal gradient at the Australian East Coast, AVS concentrations in mangrove sediments spanned $0 - 37 \mu mol/g$ ($3.2 \pm 5.7 \mu mol/g$), accounting for an average of only 2% of RIS. Consequently, CRS was the dominant form (98%) of RIS. Compiling the entire dataset (excluding dead mangrove area), pyrite reached highest values in mangroves (0 $-645 \mu mol/g$, 0 - 7.7%), followed by saltmarshes ($0 - 395 \mu mol/g$, 0 - 4.7%) and seagrasses 304 ($2.5 - 59 \mu mol/g$, 0.03 - 0.71%) (Figure 5).

305 In mangrove and saltmarsh sediments, pyrite increased with depth, whereas in 306 seagrass sediments, pyrite marginally decreased with depth (Figure 5). Furthermore, pyrite correlated with sediment organic carbon in mangroves $(0.16 - 19\%, R^2 = 0.24^{***})$, but not in 307 saltmarshes $(0.43 - 8.6\%, R^2 = 0.001)$ or seagrasses $(0.021 - 1.6\%, R^2 = 0.09)$. Reactive iron 308 reached the highest levels in mangroves (0 - 4.2%), followed by saltmarshes (0 - 2.9%) and 309 310 seagrasses (0.1 - 1.0%), and was negatively correlated with pyrite in mangroves $(R^2 =$ 311 0.17***). The redox potential in mangrove (-216 to 438 mV), saltmarsh (-48 to 364 mV), and 312 seagrass (-30 to 207 mV) sediments showed no significant correlation with pyrite (data not 313 shown).



314 315

Figure 5. Relationship between pyrite and (a) depth, (b) sediment carbon and (c) reactive iron. Boxplots of (d) 316 pyrite stocks, (e) sediment carbon stocks and (f) degree of pyritization at mangrove (n = 14), saltmarsh (n = 6)317 and seagrass (n = 2) sites. Stocks are calculated for 1 m depth. Grey areas indicate the 95% confidence intervals 318 of the regressions.

319 Pyrite stocks were three-times higher in mangroves (103 \pm 61 Mg/ha) than in 320 saltmarshes (30 \pm 30 Mg/ha) and seagrass (32 \pm 1 Mg/ha) sites (Figure 5, Table 2). In 321 saltmarshes, pyrite stocks were on average, threefold higher in cores taken closer to the water 322 edge compared to cores taken at a higher elevation in the tidal frame, whereas at mangroves 323 no difference was found. Carbon stocks, calculated for 1 m depth, in mangroves (249 ± 58 324 Mg/ha) and saltmarshes (261 \pm 86 Mg/ha), were three-times higher than in seagrasses (72 \pm 325 15 Mg/ha). On average, carbon stocks were two-times higher than pyrite stocks at mangroves 326 and seagrasses, and nine-times higher at saltmarshes. The DOP was considerably higher at 327 mangroves (0.7 ± 0.2) than at saltmarshes (0.2 ± 0.1) and seagrasses (0.3 ± 0.4) .

Site	Pyrite stock (Mg/ha)			Sediment carbon stocks (Mg/ha)			DOP (%)		
	Mangrove	Saltmarsh	Seagrass	Mangrove	Saltmarsh	Seagrass	Mangrove	Saltmarsh	Seagrass
Everglades	56						0.74		
Darwin	252			283			0.92		
Karumba	63 ± 40						0.72		
Hinchinbrook Island	113			364			0.97		
Rockhampton		2 ± 2			304 ± 10			0.01	
1770	92 ± 11			194 ± 12			0.73		
River Heads	67 ± 1	82 ± 97		223 ± 16	293 ± 16		0.26	0.36	
Sunshine Coast	107 ± 50	25 ± 25		270 ± 19	276 ± 27		0.61	0.26	
Jacobs Well	126 ± 24	45 ± 18		216 ± 56	231 ± 18		0.75	0.28	
Ballina	154 ± 52			308 ± 24			0.48		
Coffs Harbour	142 ± 7			317			0.81		
Queens Lake		24	31 ± 28		106	61 ± 4		0.31	0.05
Newcastle	122 ± 24	4 ± 3		220 ± 50	356 ± 121		0.43	0.04	
Sydney	34 ± 1		33 ± 13	182 ± 23		83 ± 5	0.85		0.59
Barwon Heads	93			204			0.36		
Average	109 ± 55	30 ± 30	32 ± 1	253 ± 59	261 ± 86	72 ± 15	0.7 ± 0.2	0.2 ± 0.1	0.3 ± 0.4

Table 2. Average pyrite stocks, sediment carbon stocks and degree of pyritisation (DOP) for 1 m depth at mangrove, saltmarsh and seagrass sites.

Drivers of mangrove pyrite stocks were investigated (Table 3). Pyrite stocks were positively correlated with aboveground biomass ($r = 0.62^*$), average annual tidal amplitude, sediment carbon stocks (r = 0.50), sedimentation rates (r = 0.47), average annual rainfall (r =0.45), latitude (r = -0.41), average annual temperature average (r = 0.25), and reactive iron within the catchment (r = 0.24). Pyrite stocks were not correlated with average surface water salinities. Table 3. Explanatory variables and Pearson correlations with pyrite stocks, variables that were used as model data inputs. Annual temperature and rainfall were averaged between 1982 and 2012 (Climate-Data.org, 2020). Average annual tidal amplitude was retrieved from Bureau of Meteorology (2020). Reactive iron was averaged for a 50 km radius around the sites (Rossel et al., 2016).

Site	Latitude	Av. annual temperature (°C)	Av. annual rainfall (mm)	Av. annual tidal amplitude (m)	Average salinity	Sediment carbon stocks (MgC/ha)	Aboveground biomass (MgC/ha)	Reactive iron (mg/g)	Sedimentation rate (cm/y)
Everglades	25	23.6	1534	0.9	27 ^a	366 ^g	71 ^g	1	0.36 ^m
Darwin	-12	27.4	1694	7.1	35 ^b	391 ^h	113 ^h	5	0.63
Karumba	-17	27.1	876	3.5		123 ⁱ	29 ⁱ	9	0.77^{i}
Hinchinbrook I.	-18	24.2	2001	3.3	35 ^b	$506^{\rm h}$	73 ^h	3	0.51
Seventeen Seventy	-24	22.1	1196	4.2	37 ^b	241 ^h	41 ^h	4	0.13
River Heads	-25	21.6	1225	3.1		223	35	5	
Sunshine Coast	-26	20.5	1788	2.0	15 ^c	270	46 ^j	8	
Jacobs Well	-27	19.9	1555	1.8	37 ^b	$272^{\rm h}$	35 ^h	5	0.27
Ballina	-28	19.7	1805	1.7	30 ^d	308	48^{j}	9	0.78^{n}
Coffs Harbour	-30	18.8	1688	1.7	15 ^e	317	52 ^j	27	0.51 ^m
Newcastle	-32	18.0	1139	1.8	33 ^b	$257^{\rm h}$	32 ^h	7	0.20
Sydney	-34	17.6	1309	1.8	$35^{\rm f}$	182	36 ^j	4	0.04^{n}
Barwon Heads	-38	14.8	666	1.2	35 ^b	271 ^h	$2^{\rm h}$	10	0.27

^aReithmaier et al. (2020); ^bSippo et al. (2016); ^cBrown et al. (2018); ^dMaher et al. (2015); ^eJeffrey et al. (2018); ^fLee and Patterson (2002); ^gJerath et al. (2016); ^hSanders et al.

339 (2016a); ⁱSippo et al. (2020); ^jSimard et al. (2019); ^kSmoak et al. (2013); ^lLogan et al. (2011); ^mConrad et al. (2017); ⁿMacreadie et al. (2012)

Along the latitudinal gradient, average SAR ranged from 0.13 - 0.63 cm/y and MAR from 0.08 - 0.27 g/cm²/y (Table 4). Pyrite accumulation and resulting TAlk production were lowest at temperate Barwon Heads ($0.04 \text{ mmol/m}^2/d$ and $0.2 \pm 0.05 \text{ mmol/m}^2/d$, respectively) and highest at tropical Darwin ($0.41 \text{ mmol/m}^2/y$ and $16 \pm 4 \text{ mmol/m}^2/d$, respectively), which showed highest MAR and pyrite concentrations. TAlk production coupled to pyrite formation is equal to 1 - 41% of the carbon burial rates, which ranged between 7 and 39 mmol/m²/d.

Table 4. Parameters required to estimate TAlk generation associated with pyrite formation and carbon burial
 rates. Values SAR and carbon burial rates were retrieved from Smoak et al. (2013).

Site	SAR (cm/y)	MAR (g/cm²/y)	Pyrite accumulation (mmol/m²/d)	Estimated TAlk production (mmol/m ² /d)	Carbon burial (mmol/m²/d)
Everglades	0.36	0.12	0.41	2 ± 0.6	34
Darwin	0.63	0.27	3.27	16 ± 4	39
Seventeen Seventy	0.13	0.08	0.23	1 ± 1.4	9
Hinchinbrook Island	0.51	0.13	1.08	5 ± 0.3	48
Jacobs Well	0.27	0.16	0.88	4 ± 1.1	21
Newcastle	0.20	0.15	0.22	1 ± 0.3	7
Barwon Heads	0.27	0.14	0.04	0.2 ± 0.05	14

348

349 4 Discussion

350 4.1 Pyrite formation in coastal vegetated habitats

Sulfate reduction rates and reactive iron availability are the key drivers impacting the 351 pyrite formation and thus the development of pyrite stocks (Berner, 1984, Figure 6). 352 353 Seagrasses typically inhabit subtidal environments, where sulfate from overlying seawater is 354 transported into their sediments via porewater diffusion and bioturbation (Chanton et al., 1987), which can limit sulfate availability and thus pyrite formation in deeper sediments. In 355 356 mangroves and saltmarshes, sulfate is resupplied during each flood tide, whereby tidal 357 pumping drives effective porewater exchange, encouraging flushing of TAlk and transporting sulfate into deeper sediment layers, facilitating sulfate reduction (Hemond et al., 1984; Sadat-358 359 Noori et al., 2017). These differences in hydrodynamics and sulfate supply likely contribute 360 to the significantly higher pyrite concentrations observed in mangroves and saltmarshes, when compared to seagrasses in our study. At the mangrove sites, average surface water 361 362 salinities were well above the level (>15) at which sulfate availability can limit sulfate reduction (2.5 - 4) (Burdige, 2011), suggesting that sulfate availability was not a limiting 363 364 factor for pyrite formation at our study sites.



365

Figure 6. Direct (bold, black) and indirect (italic, grey) drivers of pyrite formation in coastal vegetated habitats.

367 In addition to sulfate supply, sulfate reduction requires organic carbon loading in 368 excess of the aerobic respiration capacity. Coastal vegetated habitats store a large amount of organic carbon in their sediments (Mcleod et al., 2011), typically fuelling high sulfate 369 reduction rates. Berner and Raiswell (1984) stated that usually only in extremely carbon-rich 370 371 systems (>15%), factors other than organic carbon, e.g., reactive iron, limit pyrite formation. 372 In our study, sediment organic carbon exceeded 15% only at mangroves on Hinchinbrook 373 Island, whereas at most sites sediment organic carbon was below 10%, thus suggesting that 374 organic carbon might be a major factor controlling pyrite formation at coastal vegetated 375 habitats. Accordingly, pyrite was significantly correlated with sediment organic carbon in 376 both mangroves and seagrasses, underlining the importance of organic carbon on pyrite 377 formation in these systems. Similarly, previous mangrove studies found correlations between organic carbon and pyrite (Crémière et al., 2017; Ding et al., 2014; Ferreira et al., 2007b; 378 Sherman et al., 1998). The positive correlation between mangrove pyrite stocks and SAR 379 380 suggests that high SAR may limit the degradation of organic matter via aerobic carbon 381 mineralisation pathways (Berner, 1984; Raiswell & Canfield, 2012), thus providing labile carbon for sulfate reduction. At the seagrass sites, sediment carbon stocks were three times lower than that at mangroves and saltmarshes, which may contribute to the comparatively low pyrite stocks in seagrasses. Sediment organic carbon and pyrite concentrations showed no significant correlation at saltmarsh sites, suggesting that other limiting factors, such as less favourable redox conditions, might be more relevant controls on pyrite formation at the saltmarsh sites.

388 In addition to sedimentary organic carbon, vegetation itself can impact pyrite formation. Mangrove pyrite stocks were significantly correlated with aboveground biomass (r 389 390 $= 0.65^{*}$). Biomass might be a more conservative proxy for carbon availability than sediment 391 carbon stocks, which are highly heterogenous (Brown et al., 2016). Furthermore, 392 aboveground biomass can be regarded as a proxy for belowground biomass (Komiyama et 393 al., 2008), which actively influences pyrite formation. Roots may facilitate pyrite formation 394 by lowering the pH, releasing exudates, stimulating sulfate reducing bacteria and creating 395 local oxidising conditions required for partial FeS oxidation (Ferreira et al., 2007a; Giblin, 396 1988; Holmer et al., 1994; Holmer et al., 2006; Morse, 1999). Previous studies have found higher pyrite content in vegetated habitats than adjacent unvegetated sediments, highlighting 397 398 the importance of vegetation on pyrite formation (Andrade et al., 2012; Ferreira et al., 2007a; 399 Giblin, 1988; Holmer et al., 2003; Otero et al., 2009). The degree to which the vegetation 400 impacts pyrite formation varies between species, depending on root characteristics and 401 primary productivity (Holmer et al., 2006; Sherman et al., 1998).

402 In addition to sulfate reduction rates, reactive iron is a critical ingredient for pyrite 403 formation. Previous studies observed that reactive iron availability impacted pyrite formation in mangroves (Ferreira et al., 2007b; Otero et al., 2009), saltmarshes (Giblin, 1988; Morse et 404 405 al., 2007) and seagrasses (Holmer et al., 2003; Morse, 1999), which were characterised by a 406 sandy sediment texture or calcareous sediments and were thus iron-poor. Reactive iron was negatively correlated with pyrite at all coastal vegetated habitats. This can be explained by 407 408 the biogeochemical zonation of coastal sediments (Froelich et al., 1979; Johnston et al., 2011). Pyrite and S(-II) increased with depth, whereas reactive iron(III) oxides are consumed 409 and Fe²⁺ decreased under more reducing conditions associated with pyrite formation. The 410 411 DOP is a more effective measure to evaluate the effect of reactive iron on pyrite formation 412 than in situ iron concentrations. The DOP was considerably higher at mangroves (up to 0.97) 413 than at saltmarsh (up to 0.36) and seagrass (up to 0.59) sites, suggesting that only at some 414 mangrove sites pyrite formation was limited by reactive iron. At Hinchinbrook Island (DOP = 0.97) and Darwin (DOP = 0.92), sites that were characterised by high sediment organic 415 416 carbons stocks, DOP was particularly high, thus suggesting iron limitation. Furthermore, 417 mangrove pyrite stocks showed a positive correlation with average reactive iron within a 50 418 km radius around the sites, suggesting that the catchment geology also impacted pyrite 419 formation.

420 Sedimentary pyrite accumulation requires mixed redox conditions for the formation of polysulfides or the partial oxidation of FeS (Luther III et al., 1982). In coastal vegetated 421 422 habitats, roots and bioturbation can create oxidised microzones promoting pyrite formation. 423 However, intense bioturbation and high rates of primary production (and oxygen release from 424 roots) can also lead to oxidation of pyrite (Ferreira et al., 2007a; Giblin, 1988; Holmer et al., 1994; Holmer et al., 2006; Luther III et al., 1982). In intertidal mangroves and saltmarshes, 425 426 redox conditions are strongly moderated by the water level. Consequently, pyrite formation 427 can vary considerably between different geomorphological settings and locations within an 428 ecosystem (Ferreira et al., 2007b; Giblin, 1988; Machado et al., 2014; Sherman et al., 1998). At Karumba, pyrite decreased slightly with increasing distance to the ocean, which was 429

430 accompanied by an increasing redox potential. However, the proximity to the water edge (i.e. 431 tidal channel) did not generally affect measured mangrove pyrite stocks. In contrast, 432 saltmarsh pyrite stocks decreased noticeably with increasing distance from the water edge. 433 The fact that saltmarsh pyrite stocks were threefold lower than mangrove pyrite stocks, despite equal carbon stocks and lower DOP, is likely due to more oxidising conditions in the 434 upper sediment layers, since saltmarshes occupy spaces higher in the tidal frame than 435 436 mangroves and have therefore a shorter hydroperiod. This is supported by the change in pyrite concentrations going down core in saltmarshes, where pyrite was close to zero in the 437 upper sediment layers and increased abruptly after around 40 - 80 cm (Figure 5). 438

439 Climatological and physical factors indirectly influence pyrite formation via their impacts on sulfate reduction and reactive iron availability. For example, mangrove pyrite 440 441 stocks were significantly correlated with the tidal amplitude ($r = 0.57^*$). Higher tidal amplitude increases porewater exchange (Tait et al., 2016), thereby resupplying sulfate, 442 443 removing aqueous reaction products and transporting allochthonous organic carbon and reactive iron through the sediments. Furthermore, mangrove pyrite stocks were also 444 positively correlated with average annual temperature and rainfall, which affect sedimentary 445 446 organic carbon and aboveground biomass (Hutchison et al., 2014; Sanders et al., 2016a). 447 Moreover, microbial sulfate reduction is highly temperature dependant (Robador et al., 2016; 448 Westrich & Berner, 1988). Increasing rainfall drives weathering rates and sediment transport, 449 and thus influences reactive iron supply from surrounding catchments (Kendall et al., 2012).

450

4.2 Mangrove pyrite formation represents an overlooked blue carbon sink

451 The blue carbon paradigm has focused primarily on the role of coastal vegetated 452 ecosystems being hotspots of organic carbon burial and subsequently large sedimentary 453 carbon stocks, whereas TAlk production has been largely overlooked (Maher et al., 2018). 454 During sulfate reduction, organic carbon is converted into bicarbonate ions, some of which 455 are exported from mangroves to the ocean via tidal porewater exchange (Krumins et al., 2013; Sippo et al., 2016), whereas sedimentary pyrite is sequestered in situ. This spatial 456 457 decoupling of two key products of sulfate reduction (pyrite and bicarbonate ions) leads to a 458 net generation of TAlk and generates a long-term carbon sink in the form of marine bicarbonate. As such, we argue that the blue carbon framework should incorporate a more 459 holistic biogeochemical perspective which encompasses not only in situ sedimentary organic 460 461 carbon sequestration, but also pyrite formation and its attendant TAlk export. This is 462 supported by our results that show TAlk production associated with pyrite formation can account for up to 42% of the organic carbon burial rate and represents therefore a 463 quantitatively relevant carbon sink. 464

465 At the Everglades and Karumba, porewater TAlk increased simultaneously with S(-II) and pyrite, highlighting the importance of pyrite formation for TAlk production. Sherman et 466 467 al. (1998) also observed a significant correlation between pyrite and TAlk in mangrove 468 sediments, but the correlation was restricted to deeper sediments, suggesting that TAlk in surface sediments was either exported by tidal flushing or driven by other processes. At the 469 470 Everglades National Park and at mangrove sites near Karumba, porewater TAlk was on 471 average six-times higher than average TAlk of seawater (2300 µmol/kg; Millero et al., 1998), 472 indicating that mangrove sediments can act as a TAlk source to coastal waters, since tidal 473 pumping drives effective porewater exchange (Tait et al., 2016).

474 We calculated the TAlk production coupled to pyrite formation and compared it to 475 published lateral TAlk export rates (Figure 7). A significant linear correlation was found for 476 Barwon Heads, Jacobs Well, Hinchinbrook Island and Darwin. In contrast, Newcastle, 477 Seventeen Seventy and the Everglades had disproportionally high TAlk export rates despite 478 apparently low TAlk production coupled to pyrite formation. The high TAlk export rates might be due to a range of alternative TAlk producing processes. For example, at the 479 480 Everglades, mangroves populate a large carbonate platform and therefore carbonate dissolution contributes substantially to TAlk production (Ho et al., 2017). At Newcastle, high 481 482 denitrification rates caused by high nutrient freshwater inputs (Maher et al., 2016) may 483 decouple lateral TAlk export and pyrite formation. Being located in the dry tropics, 484 Seventeen Seventy had the lowest carbon stocks and slowest SAR, which might have 485 favoured other carbon decomposition processes over sulfate reduction. Overall, our results 486 and analysis suggest that pyrite formation is only a robust proxy for total TAlk production 487 and export if sulfate reduction is the dominant TAlk producing process.



488

Figure 7. Mangrove TAlk export is plotted as a function of TAlk production coupled to pyrite formation. A
linaer regression is shown for Barwon Heads, Jacobs Well, Hinchinbrook Isalnd and Darwin. Export values
have been retrived from Reithmaier et al. (2020) (Everglades) and from Sippo et al. (2016) (remaining sites).

492 An important observation is that lateral TAlk export was ~ eight-fold higher than the 493 estimated TAlk production coupled to pyrite formation (Figure 7). Firstly, this discrepancy 494 might be a consequence of the contrasting time scales of TAlk production and export. 495 Production of TAlk coupled to pyrite formation integrates several decades, whereas the 496 measured TAlk export rates presented here for comparison were determined over two tidal 497 cycles have been found to vary seasonally (Ho et al., 2017; Maher et al., 2013) and over 498 spring-neap cycles (Taillardat et al., 2018), suggesting short-term measurements likely do 499 not capture longer term rates. Secondly, the discrepancy might be due to additional TAlk 500 production processes, such as denitrification, manganese reduction, iron reduction and 501 carbonate dissolution (Krumins et al., 2013). It is also very likely, that a proportion of sulfate 502 reduction is not coupled to pyrite formation (Berner, 1984), with some oxidation of exported 503 reduced metabolites occurring outside of the mangroves, and therefore not accounted for in 504 the lateral exchange method of Sippo et al. (2016). Consequently, future carbon sink 505 estimates based on lateral TAlk exports should also assess export of reduced metabolites to 506 provide a net estimate.

507 Sulfate reduction only contributes to net TAlk production if the reduced sulfur is 508 spatially decoupled from bicarbonate ions and prevented from re-oxidising in a manner that 509 consumes produced bicarbonate. In addition to pyrite formation, other processes can 510 theoretically remove sulfide from mangrove sediments and result in pyrite being an 511 underestimate of net TAlk production rates. For example, mangroves can remove reduced sulfur by assimilating and storing sulfide in their plant tissue (Fry et al., 1982; Okada & 512 513 Sasaki, 1995). To the best of our knowledge, sulfide uptake rates by mangrove has not yet 514 been quantified. Alongi et al. (2003) compiled mangrove tree sulfur content in Avicenia marina and Rhizophera stylosa stands and found an average of 0.6 and 2.1 Mg S/Ha, which, 515 516 assuming all sulfur was associated with sulfide uptake, would only increase net TAlk 517 production by between 0.4 and 11% for our sites.

518 In addition to plant uptake, reduced sulfur may be removed from the sediment by 519 outgassing as hydrogen sulfide gas (H₂S) (Castro & Dierberg, 1987; Ganguly et al., 2018). 520 There are limited forest-scale estimates of H₂S emissions. However, a study in the 521 Sundarbans mangrove forest found emissions of 0.3 g $S/m^2/y$ (Ganguly et al., 2018). If these emissions are representative of mangrove forests more generally, such gaseous H₂S flux 522 523 would only result in a TAlk production (unaccounted for by pyrite) of 0.1 mmol/ m^2/d an 524 order of magnitude smaller than our pyrite-based estimates of TAlk production. Currently, 525 sulfur removal by plant uptake and hydrogen sulfide emissions are not sufficiently quantified 526 to constrain their effect on net TAlk production. However, this analysis suggests that their 527 effect is likely to be minor compared to pyrite stocks.

528 Production and export of TAlk coupled to pyrite formation represent not only a blue 529 carbon sink, but might also buffer coastal acidification (Sippo et al., 2016). Conversely, when 530 pyrite is oxidised, net TAlk production can be reversed, resulting in acidity release that 531 offsets blue carbon sinks. At Karumba, pyrite stocks were lower at the dead mangrove area 532 compared to the living mangrove area, suggesting pyrite loss. At the living area, pyrite stocks 533 were significantly correlated to groundwater TAlk, indicating that pyrite formation was 534 linked to TAlk generation. Assuming similar pyrite concentrations in living and dead areas prior to the dieback, the dieback reversed the TAlk generation, releasing 54 mol/m² of acidity 535 536 through the oxidation of pyrite. If pyrite was gradually lost over time, then 56 mmol/ m^2/d of 537 TAlk was lost as CO₂ emissions between the dieback and our sampling. This highlights that 538 mangrove sediment disturbance leading to pyrite oxidation can reverse the TAlk carbon sink 539 coupled to pyrite formation, releasing carbon to the atmosphere.

540

4.3 Global pyrite stocks and resulting alkalinity production in mangroves

From our data we constructed a global model for mangrove pyrite stocks and the associated TAlk production. Although sampling covered a broad range of climatic zones, it was limited to sites in Australia and the USA. Therefore, future research is encouraged to validate our model by quantifying pyrite stocks in other parts of the world, since to our knowledge no other mangrove pyrite stocks have been published. Despite the limitations of our model, it is a useful first order estimate to determine the general importance of alkalinity production coupled to pyrite formation on a global level.

548 Our model explained 78% of the variability in the observed mangrove pyrite stocks (Figure 549 8). The model data equation $(-459.360057 - 2.348824 \times \text{Temperature} (^{\circ}\text{C}) + 0.176380 \times$ 550 Tidal amplitude (cm) + 89.656683 × ln(Sediment carbon stock (Mg/ha)) + 7.708681 × 551 ln(Aboveground biomass (Mg/ha)) - 0.614195 × Latitude - 0.003740 × Rainfall (mm) + 552 35.784984 × ln(Catchment iron (mg/g)) is based on data presented in Table 3. By combining 553 our model with published global datasets for key model parameters we estimate that mangroves store in total 2.1 (25% to 75% percentile range of 1.8 - 2.5) Pg of pyrite globally to a depth of 1 m with an average of 155 (range = 128 - 182) Mg/ha (Figure 9).



556

557 **Figure 8.** Correlation between observed and modelled mangrove pyrite stocks. The grey area shows the 95% confidence intervals of the regression. The regression has a slope of one.

559



560100°0'0"W60°0'0"W20°0'0"W60°0'0"E100°0'0"E140°0'0"E180°0'0"561Figure 9. Global map of mangrove pyrite stocks and detailed maps of the Everglades, the Sundarbans and562Malaysia.

Currently, no high-resolution global maps for SAR exist, therefore the TAlk 563 production rate is limited to an empirical calculation. Multiplying the global average pyrite 564 565 stocks by the global average SAR for mangroves (0.49 cm/y) determined by Alongi (2012), and converting it to TAlk production yields a total TAlk production that is coupled to global 566 567 pyrite formation of 0.44 Tmol/y (range = 0.37 to 0.52 Tmol/y). This TAlk production rate is 568 within the broad range estimated by Hu and Cai (2011), who used a range of sediment C/S ratios and carbon burial rates to estimate that pyrite formation in coastal vegetated habitats 569 results in a net TAlk production of 0.1 - 1.1 Tmol/y. Our estimated global average TAlk 570 production rate (3.2 mol/m²/y, range = 2.7 - 3.8 mol/m²/y), is equivalent to 24% (range = 19 571 -27%) of the global organic carbon burial rate (14 mol/m²/y) within mangrove sediments 572 (Breithaupt et al., 2012), highlighting the importance of including this mode of TAlk 573 574 generation into future blue carbon budgets.

575 **Conclusion**

576 The majority of blue carbon research has focused on organic carbon stocks, whereas 577 TAlk production and export has been less investigated. Quantifying pyrite stocks and the 578 associated TAlk production in coastal vegetated habitats, we found that alkalinity production 579 coupled to pyrite formation might represent a significant blue carbon sink. However, the 580 long-term production rates of pyrite are an order of magnitude smaller than short-term 581 measured TAlk export rates, suggesting that the timescales of measurement, and 582 methodology used need to be adequately addressed. While more research is required to 583 understand the drivers and relevance of this process, we argue that pyrite accumulation 584 should be included in the blue carbon paradigm as is represents a long-term carbon sink.

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