Benthic Alkalinity and DIC Fluxes in the Rhône River Prodelta Indicating Decoupled Aerobic and Anaerobic Processes

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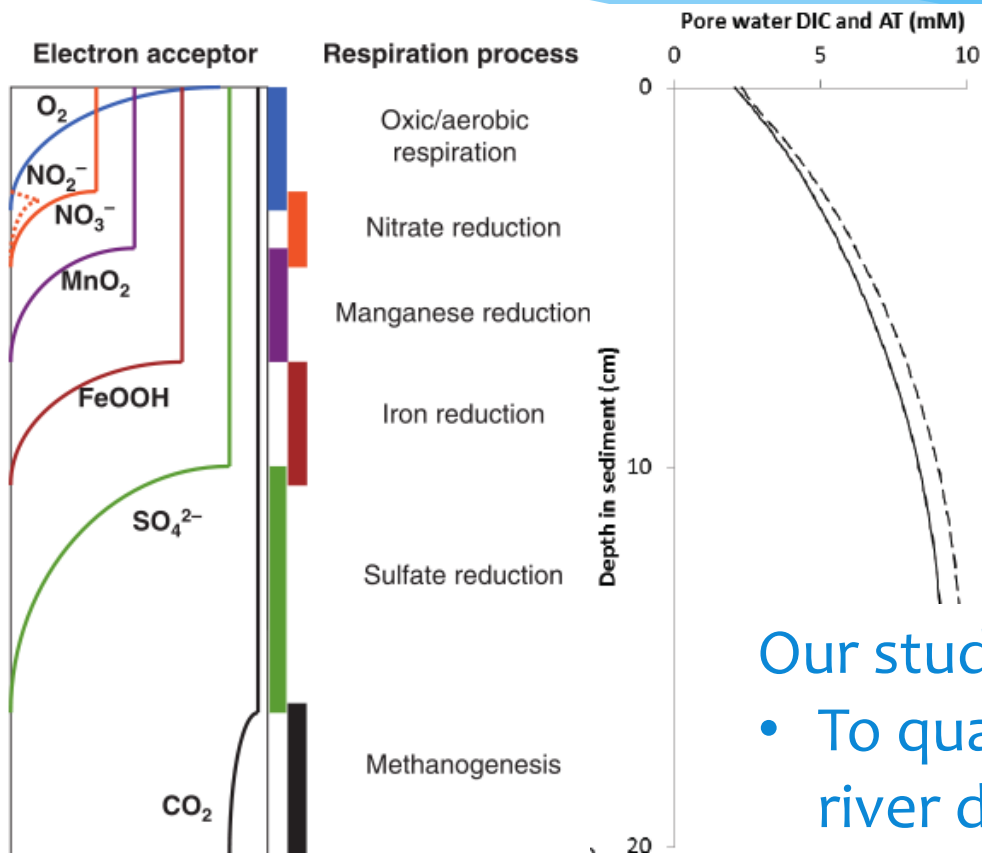
3: IFREMER, France

LSCE

Georgia Tech

Ifremer

Rationale

* Ocean Acidification (OA) is a growing concern with rising atmospheric CO_2 and in situ acidification by OM mineralization

* We have extensive knowledge about atmospheric CO_2 invasion which drives OA, maybe less about in situ remineralization
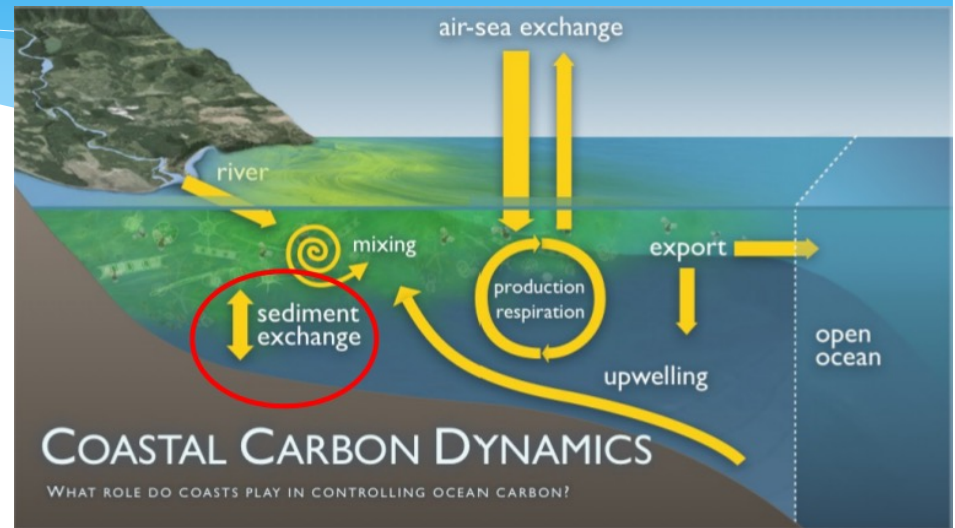
* Yet, little is known concerning mitigating processes that could increase buffering effect such as alkalinity production/fluxes in the ocean, especially from sediments

* It has been proposed by Thomas et al. (BG, 2009) and Krumins et al. (BG, 2013) that sediment can contribute to the alkalinity budget of the coastal ocean

Background: Organic matter mineralization in sediments and DIC/TA production

Electron acceptor

O_2
NO_2^-
NO_3^-
MnO_2
$FeOOH$
SO_4^{2-}
CO_2

Respiration process

Oxic/aerobic respiration

Nitrate reduction

Manganese reduction

Iron reduction

Sulfate reduction

Methanogenesis

Pore water DIC and AT (mM)

Depth in sediment (cm)

- Large production of DIC in coastal sediments
- Anaerobic processes produce large alkalinity concentrations
- Oxidation of reduced product can consume all produced alkalinity

Our study objectives were:
- To quantify the DIC/TA fluxes in river delta sediments
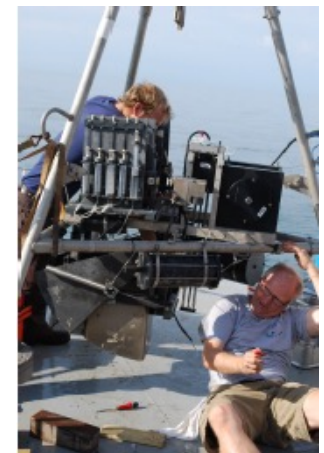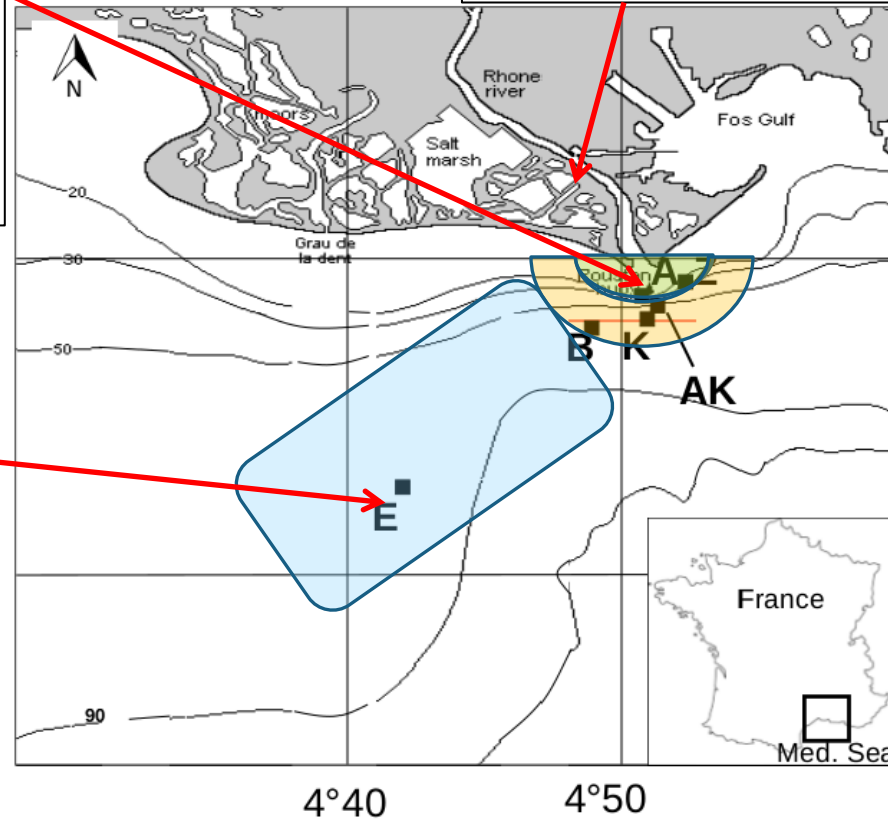- To identify the processes which generate these fluxes

Study area: the Rhône delta and NW Med Sea

Station A and Z:
prodelta
Characteristics:
Large mineralization,
large sedimentation
rate (30cm/yr)

Rhone River:
1700 m3/s
5-10 Mt sediments

Station E:
Continental shelf
Characteristics:
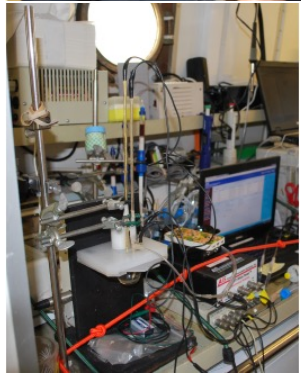Low mineralization,
low sedimentation
rate (0.1 cm/y)

- Use of in situ methods for measuring fluxes, i.e. benthic chambers
- Porewater and solid profiles: polarographic electrodes + DIC, Alk, SO4, Fe, Mn, NH4

In situ measurements: benthic fluxes and porewater profiles
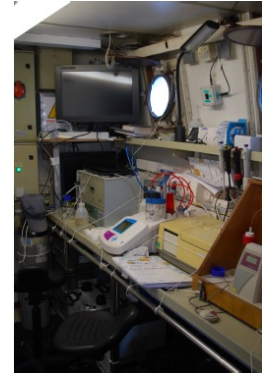
In situ benthic chambers: fluxes
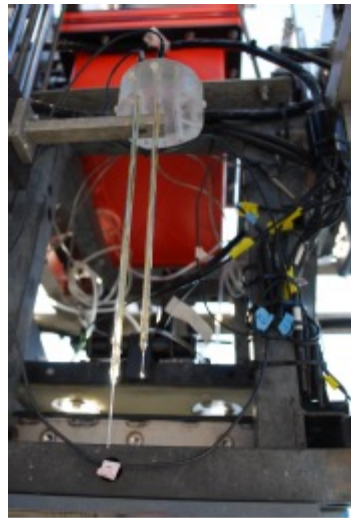
In situ micro-electrodes: O2 and pH
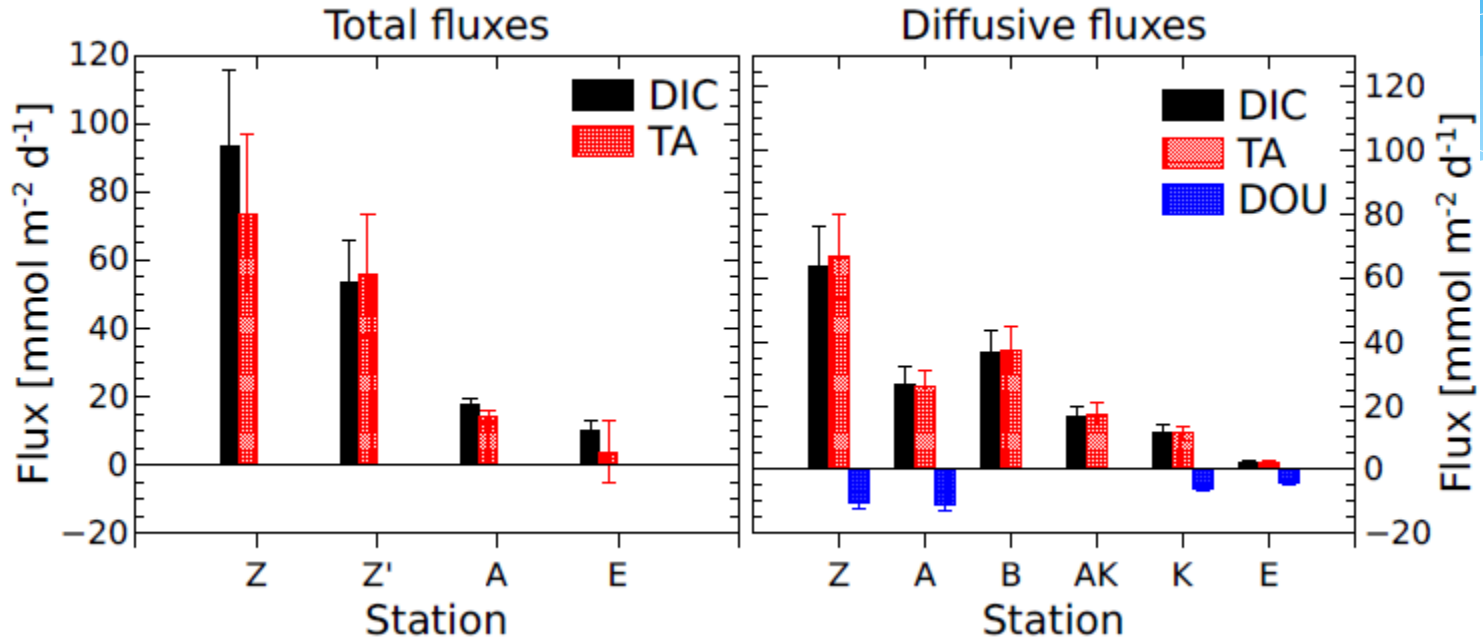

Complemented with onboard and laboratory measurements:
- Voltametric profiles using polarographic electrodes
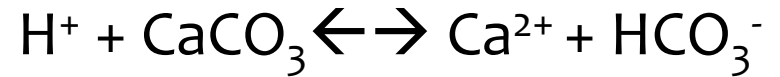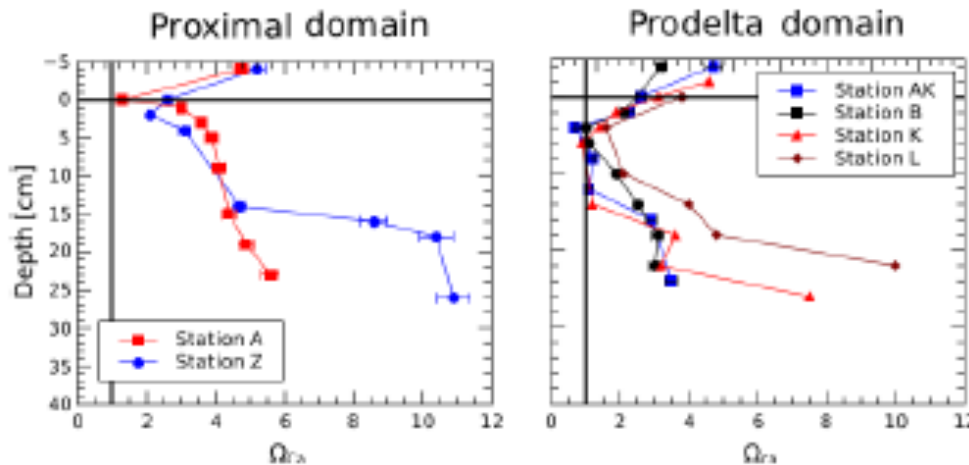- DIC, Alk, SO4, Fe, Mn, NH4 on porewater extracted by Rhizons

Benthic fluxes

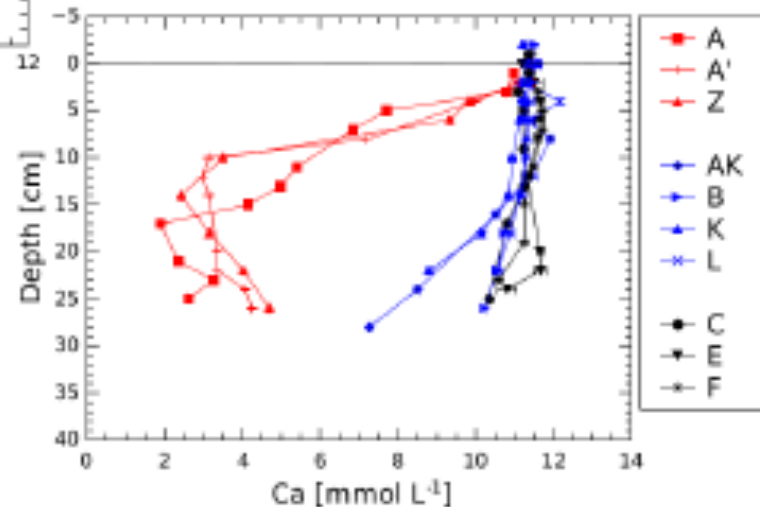- Nearshore sediments are a strong source of alkalinity and DIC

- The intensity of the fluxes decreases offshore

- In nearshore region, DIC and TA fluxes are decoupled from O_2 fluxes

Carbonate dissolution?

$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^-$$
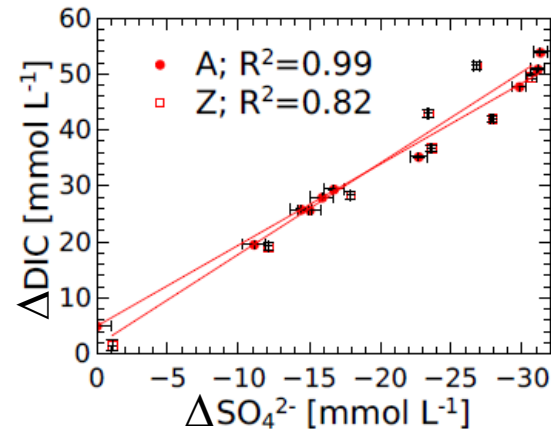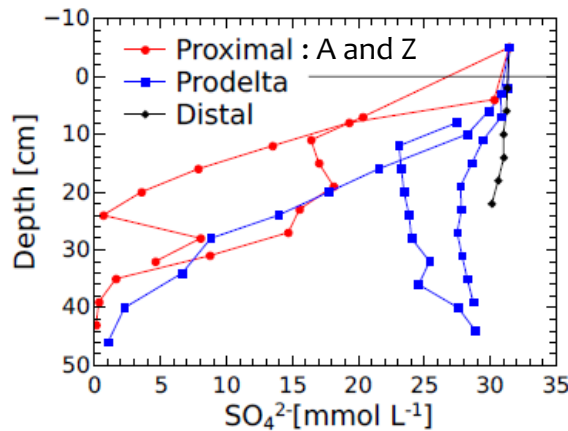
- Porewaters are supersaturated with $CaCO_3$
- Ca2+ profiles show no dissolution but rather precipitation → this should decrease alkalinity

Alkalinity and DIC profiles in delta sediments…
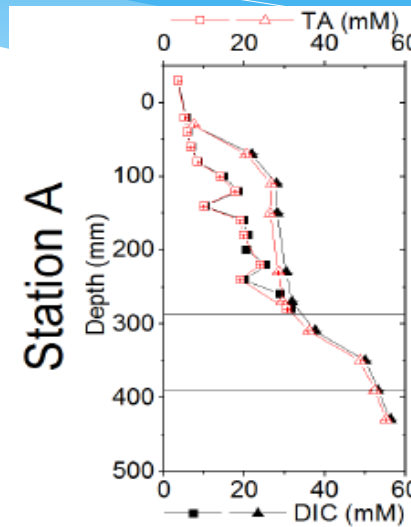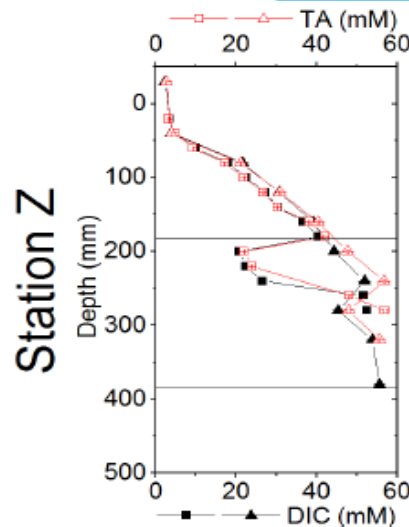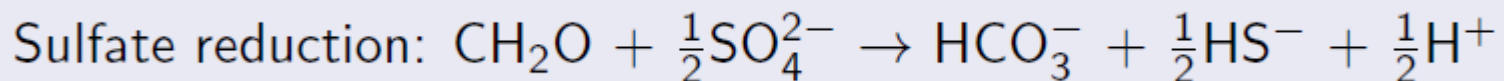

## …explained by large sulfate reduction

Rassmann et al., 2016, BG

Sulfate reduction: $CH_2O + \frac{1}{2}SO_4^{2-} \rightarrow HCO_3^- + \frac{1}{2}HS^- + \frac{1}{2}H^+$

Stoechiometric reactions

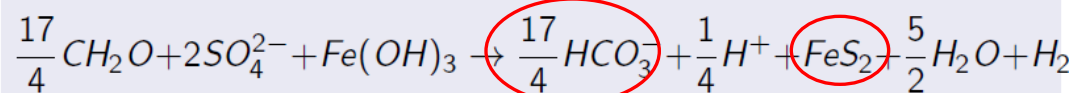|		Reaction	ΔTA / ΔDIC
	Carbonate chemistry		
R1	CO_2 dissolution	$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow HCO_3^- + H^+ \longleftrightarrow CO_3^{2-} + 2H^+$	
R2a	Carbonate dissolution	$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$	$+2/1$
R2b	Carbonate precipitation	$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$	$-2/-1$
	Aerobic reactions		
R3	Aerobic mineralization	$CH_2O + O_2 \rightarrow HCO_3^- + H^+$	$0/1$
R4	Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	$-2/0$
R5	Iron oxidation	$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$	$-8/0$
R6	Manganese oxidation	$2Mn^{2+} + O_2 + 4HCO_3^- \rightarrow 2MnO_2 + 4CO_2 + 2H_2O$	$-4/0$
	Anaerobic reactions		
R7	Nitrate reduction	$CH_2O + 0.8NO_3^- + 0.8H^+ \rightarrow CO_2 + 0.4N_2 + 1.4H_2O$	$0.8/1$
R8	Manganese reduction	$CH_2O + 2MnO_2 + 3H^+ \rightarrow HCO_3^- + 2Mn^{2+} + 2H_2O$	$4/1$
R9	Iron reduction	$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow HCO_3^- + 4Fe^{2+} + 10H_2O$	$8/1$
R10	Sulfate reduction	$CH_2O + \frac{1}{2}SO_4^{2-} \rightarrow HCO_3^- + \frac{1}{2}HS^- + \frac{1}{2}H^+$	$1/1$
R11	FeS precipitation	$Fe^{2+} + HS- \rightarrow FeS + H^+$	$-2/0$
R12	FeS precipitation with sulfate recycling	$8Fe(OH)_3 + 9HS^- + 7H^+ \rightarrow 8FeS + SO_4^{2-} + 20H_2O$	$-2/0$
R14	Pyrite precipitation	$8Fe(OH)_3 + 15HS^- + SO_4^{2-} + 17H^+ \rightarrow 8FeS_2 + 28H_2O$	$2/0$
R15	Anaerobic methane oxidation	$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$	$2/1$
R16	Methanogenesis	$CH_2O \rightarrow \frac{1}{2}CH_4 + \frac{1}{2}CO_2$	$0/0.5$

Coupling of iron and sulfur cycles
Station A & Z

[HS-] is insignificant although sulfate reduction is complete
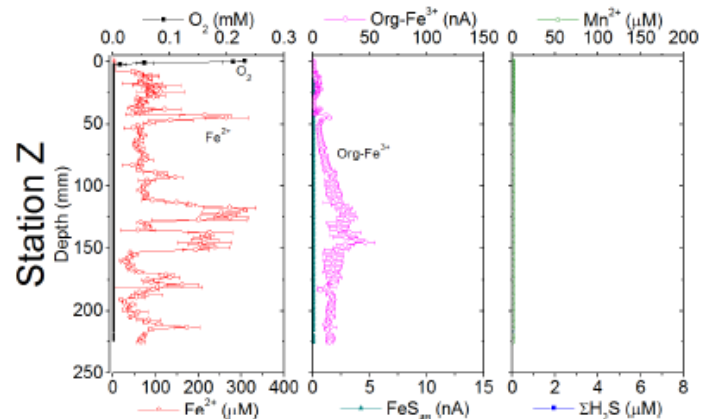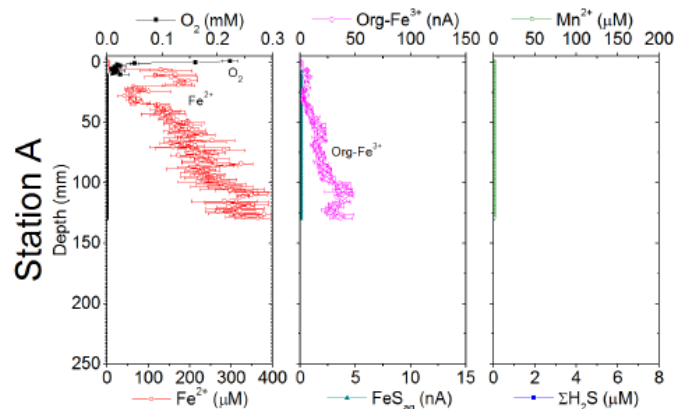
Rassmann et al., in rev. Mar. Chem

[Fe²⁺] is very large indicating iron oxide reduction coupled to organic matter mineralization or sulfide oxidation

→ Large precipitation of FeS and FeS₂ accompanied by alkalinity net production

$$\frac{9}{4}CH_2O + SO_4^{2-} + Fe(OH)_3 \rightarrow \frac{9}{4}HCO_3^- + \frac{1}{4}H^+ + FeS + \frac{5}{2}H_2O$$

$$\frac{17}{4}CH_2O + 2SO_4^{2-} + Fe(OH)_3 \rightarrow \frac{17}{4}HCO_3^- + \frac{1}{4}H^+ + FeS_2 + \frac{5}{2}H_2O + H_2$$
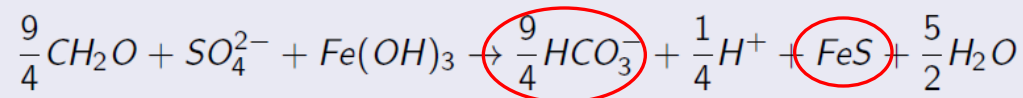
Precipitation and burial of iron sulfide
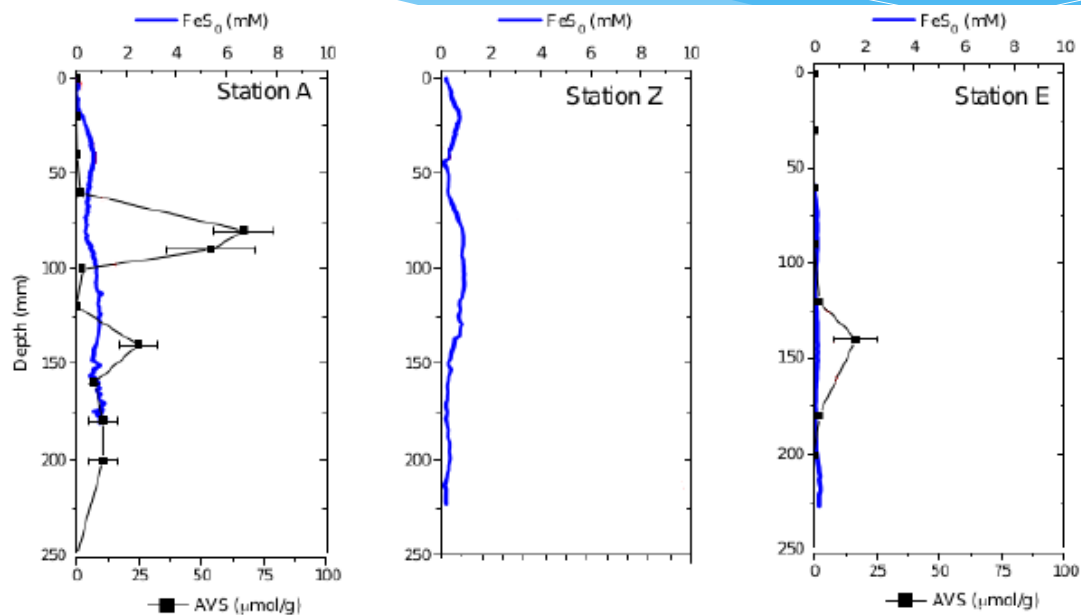
Large concentrations of particulate FeS with FeS_0 as precursor of precipitation

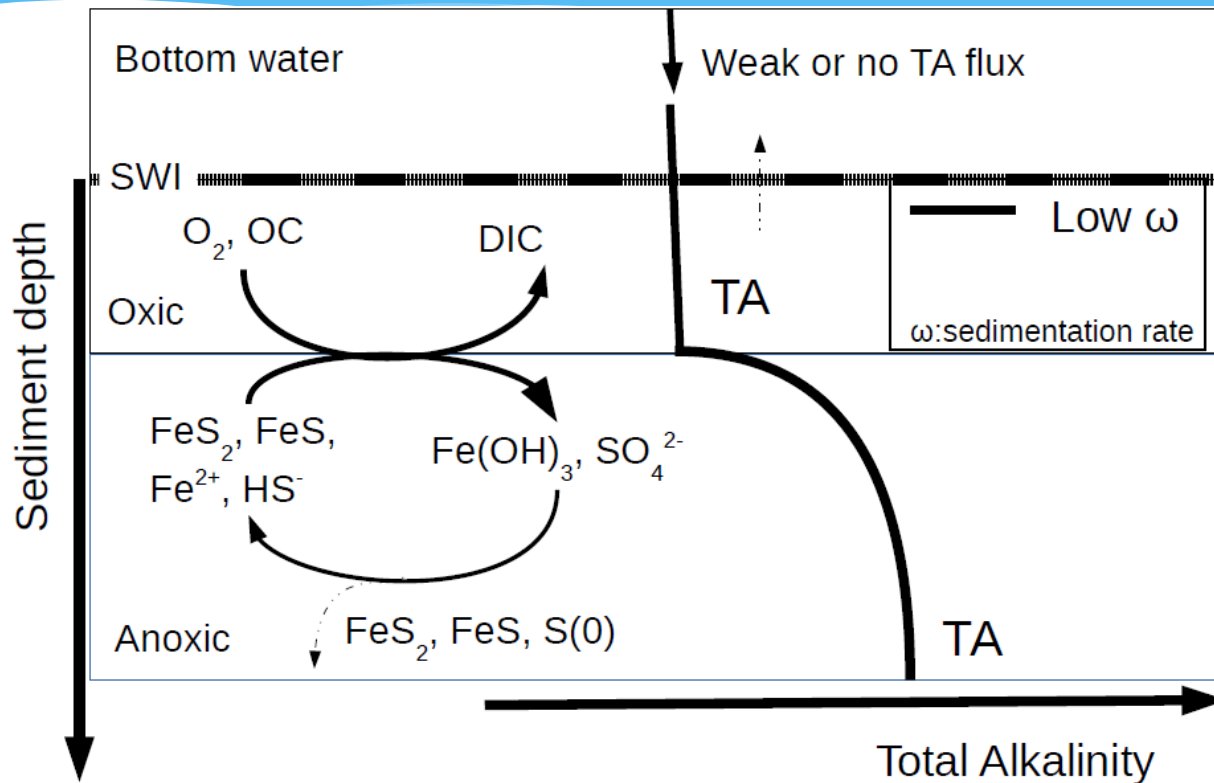| Burial FeS	A and Z	E
Sedimentation rate (cm yr^{-1})	30	0.1
Mean AVS (μmol g^{-1})	19.5 ± 5	9 ± 2.3
Burial FeS (mmol S m^{-2} d^{-1})	12.5 ± 4	0.02 ± 0.01

Conceptual model: alkalinity generation with burial of reduced species

- Low sedimentation rate coupled to limited sulfate reduction induce little or no alkalinity flux (only linked to denitrification)

- Large sedimentation rates with intense FeS production create a sink of reduced products and a source of alkalinity to the BW

Alkalinity balance in prodelta sediments

Alkalinity balance	A and Z (prodelta)	E (Contin. Shelf)
Sedimentation rate (cm yr^{-1})	30	0.1
Mean AVS (µmol g^{-1})	19.5 ± 5	9 ± 2.3
Burial FeS (mmol S m^{-2} d^{-1})	12.5 ± 4	0.02 ± 0.01
Alkalinity source (FeS prod - mmol m^{-2} d^{-1})	25 ± 8	0.04 ± 0.01
Alkalinity flux (Benthic C. - mmol m^{-2} d^{-1})	47.8 ± 30.4	3.9 ± 9

- In the nearshore region (A&Z), burial of FeS is in the same order of magnitude as alkalinity flux
- On the shelf (E), they are decoupled.

Conclusion

- Large benthic alkalinity and DIC fluxes arise from the Rhône River prodelta

- These fluxes are related to large FeS precipitation and burial: they show the same order of magnitude

- River deltas are prone to anoxic mineralization and can potentially produce and bury FeS as :

  - They receive large amounts of organic material

  - Significant terrigenous material with iron is dicharged

  - They exhibit large sedimentation rates

- There might be a significant source of Alkalinity from river delta sediments

- In RiOMars (River-dominated Ocean Margins) this may limit acidification created by anthropogenic CO_2 invasion and in situ respiration

Acknowledgments

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