Supplementary Information for

Dissolved Inorganic Carbon Pump in Methane Charged Shallow Marine Sediment Systems: State of the Art and New Model Perspectives

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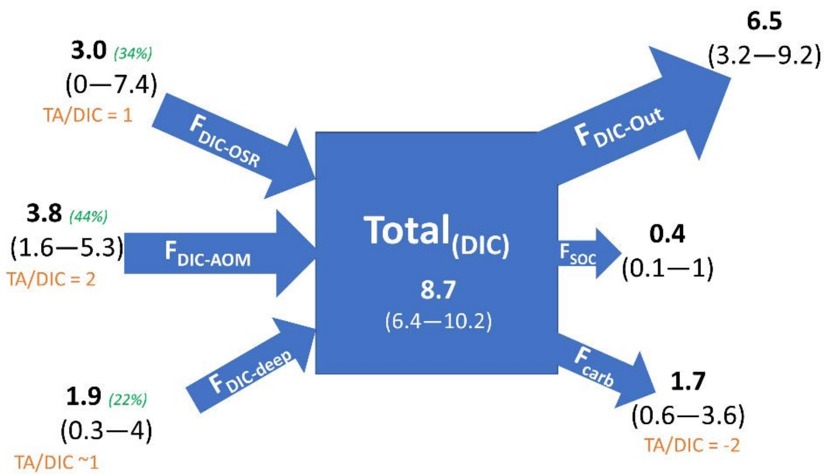
1. TA/DIC of the DIC Outflux



Supplementary Figure 1: DIC cycling at SMTZ with % flux contribution of AOM, OSR and Deep-DIC flux and TA/DIC values (modified from Figure 4 main text).

The ratio of Total Alkalinity (TA) to DIC (TA/DIC) for AOM and OSR is 2 and 1 respectively [Supp. Table 1, *Wurgaft et al.*, 2019]. Deep-DIC flux would have a TA/DIC of 1 assuming the simple equation in table 1. Additional alkalinity sourcing to this deep-DIC can occur due to NH_4 production coupled to organic matter degradation in methanogenic sediments (Wallmann et al., 2008; Solomon et al., 2014; Torres et al., 2020) as well as from DIC flux from deep subsurface due to alteration of continental crust alteration (Meister et al., 2011). With limited data on global trend of alkalinity fluctuations of deep-DIC, we assume a conservative TA/DIC value of 1 in this calculation. Authigenic carbonate precipitation at the SMTZ can consume two moles of bicarbonate (Eqn. 4) and reduce the TA/DIC by a factor of two.

Supplementary Table 1: TA/DIC variation of carbon cycling processes at diffusive setting

Process	Equation	TA Increase	DIC Increase	TA/DIC
AOM	$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$	2	1	2
OSR	$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$	2	2	1
MSiW (Deep-DIC)	Cation−rich silicate+CO_2 → cation−depleted silicates+HCO_3^-+ Cations	1	1	1
Carbonate Precipitation	$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O$	-2	1	-2
Iron Sulfide Precipitation	$H_2S + 2/5Fe_2O_3 \rightarrow 2/5FeS_2 + 1/5\ FeS + 1/5\ FeO + H_2O$	-	-	-

Supplementary Table 2: variation in TA/DIC for DIC outflux at diffusive setting under complete sulfide burial and varying ranges of parameters used in Eqn. 6 and table 1 in the main article. Values in red indicates settings with DIC outflux contributing as CO_2 to water column and values in green indicates DIC outflux contributing as Alkalinity.

Setting	**DIC Input** (Tmol yr^{-1}) (Total CH_4 flux = 3.8; Total SO_4^{2-} flux = 5.3)			Total DIC (Tmol yr^{-1})	TA/DIC of			
	DIC via AOM	DIC via OSR	DIC via deep flux		Net DIC at SMTZ	DIC outflux with F_{carb}[¶] 10	20	25
MAX TA/DIC Setting*	5.3	0	1.1	6.4	1.83	1.63	1.43	1.33
Avg TA/DIC Setting§	3.8	3	1.9	8.7	1.44	1.24	1.04	0.94
MIN TA/DIC Setting#	1.6	7.4	1.2	10.2	1.16	0.96	0.56	0.06

¶ $TA/DIC_{(DIC\text{-}Out)} = 2(*\%_{AOM\text{-}DIC}) + 1(*\%_{OSR\text{-}DIC}) + 1(*\%_{Deep\text{-}DIC}) - 2\ (F_{carb})$

*Max TA/DIC Setting: AOM:OSR = 100:0 for total consumption of SO_4^{2-} flux, Deep-DIC = 20% CH_4 flux

§Average TA/DIC Setting: AOM:OSR = 70:30 for total consumption of SO_4^{2-} flux, Deep-DIC = 50% CH_4 flux

#Min TA/DIC Setting: AOM:OSR = 30:70 for total consumption of SO_4^{2-} flux, Deep-DIC = 75% CH_4 flux

Supplementary Table 3: Comparison of global DIC flux values from the SMTZ based on CH_4 flux estimates from Egger et al (2018), Wallmann et al. (2012) and Hinrichs and Boetius (2002). SO_4^{2-} flux values are calculated using the 1:1.4 ratio for CH_4: SO_4^{2-}.

Region (water depth (m))	CH_4 flux (Tmol yr^{-1})	SO_4^{2-} flux* (Tmol yr^{-1})	DIC Via AOM (Tmol yr^{-1})	DIC via OSR (Tmol yr^{-1})	DIC from deep sediments (Tmol yr-^{1})	Total DIC at SMTZ (Tmol yr^{-1})	DIC sequesterd via Carbonates (Tmol yr^{-1})	DIC sequesterd via SOM (Tmol yr^{-1})	DIC Out (Tmol yr^{-1})
Hinrichs and Boetius (2002)	19	26.6	19	15.2	9.5	43.7	8.7	2.2	32.8
Wallmann et al., (2012)	1.2	1.7	1.2	1.0	0.6	2.8	0.6	0.1	2.1
Egger et al., (2018)	3.8	5.3	3.8	3.0	1.9	8.7	1.7	0.4	6.6
Range	**1-19**	**2-27**	**1-19**	**1-15**	**1-3**	**3-44**	**1-9**	**0-2**	**2-33**
			AOM = 100% of CH_4 flux		Fdeep DIC = 50% of CH_4 flux		Fcarb = 20% Of DIC at SMTZ	FSOM = 5% Of DIC at SMTZ	FDIC out =75% Of DIC at SMTZ

*SO_4^{2-} flux =1.4 * CH_4 flux

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