Supplementary Material

Controlling factors on patterns of dissolved organic carbon and volatile fatty acids in a submarine mud volcano offshore southwestern Taiwan

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# Rate laws of microbial reactions

Rate laws of five reactions considered in our modeling for individual compounds were described in accordance with the Monod kinetics and stoichiometric relationships (Burdige et al., 2016; Vanneste et al., 2011; Wallmann et al., 2006) and were shown in Table S3. The rate expressions for the six species targeted are listed in Table S4. KiSO4 is the inhibition constant for the initiation of methanogenesis, and assumed to be the same as Khalf-SO4 (0.5 mM); Khalf-CH4 is the half-saturation constant for methane and assumed to be 5 mM (Nauhaus et al., 2002; Vavilin, 2013; Wegener and Boetius, 2009); [CH4] and [SO42-] are the concentrations of methane and sulfate in the porewater; $R\_{AOM}^{MAX}$ is the theoretical maximum AOM rate obtained by fitting the sulfate profile (set as 2 mM yr-1); $R\_{CP}$ is a function of depth ($x$) and assumed to be a Gaussian function (Burdige et al., 2016); $x\_{cp}$ is the sediment depth of maximum $R\_{CP}$ and was assumed to be close to the depth of the SMTZ; $s\_{cp} $ is the parameter defining the width of the Gaussian function for the depth distribution of $R\_{CP}$; $R\_{CP}$ was determined by fitting the Ca2+ and Mg2+ porewater data through varying $R\_{CP}^{MAX}$, $x\_{cp}$ and $s\_{cp}$. $rN$ is a parameter that converts nitrogen concentrations in unit of wt.% N to mM (Burdige et al., 2016). Details of the parameters used in the modeling and the parameters for best fittings are shown in Table S5.

# Supplementary Figures and Tables

## Supplementary Tables

##### Table S1. Concentrations raw data of dissolved manganese, bromide, ammonium, organic acids, and DOC.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| site | depth (cm) | Mn (M) | Br- (mM) | NH4+ (mM) | lactate (M) | formate (M) | acetate (M) | DOC (M) | DOC/NH4+(M/M) |
| A2-2 | 0 | 3  | 0.70 | 0.03 |  | 4 | 18 | 250 | 7.5 |
|  | 16 | 2  | 0.77 | 0.07 |  | 5 | 4 | 110 | 1.7 |
|  | 46 | 1  | 0.75 | 0.06 |  | 5 | 15 | 340 | 6.1 |
|  | 76 | 1  | 0.73 | 0.06 | 9 | 17 | 24 | 620 | 10.1 |
|  | 106 | 1  | 0.76 | 0.03 |  | 8 | 19 | 380 | 11.4 |
|  | 136 |   | 0.75 | 0.06 |  | 4 | 17 | 350 | 6.3 |
|  | 166 |   | 0.73 | 0.06 |  | 4 | 11 | 300 | 5.4 |
|  | 196 |  | 0.73 | 0.12 |  | 2 | 18 | 740 | 6.1 |
|  | 226 |  | 0.75 | 0.14 | 4 | 10 | 36 | 470 | 3.4 |
|  | 256 |  | 0.73 | 0.08 |  | 6 | 14 | 370 | 4.4 |
|   | 286 |  | 0.60 | 0.22 |  | 3 | 39 | 740 | 3.3 |
|  | 316 |  | 0.58 | 0.25 |  | 3 | 18 | 440 | 1.8 |
|  | 346 |  | 0.40 | 0.48 |  | 5 | 32 | 410 | 0.8 |
|  | 376 |  | 0.28 | 0.40 |  | 9 | 39 | 470 | 1.2 |
|  | 406 |  | 0.27 | 0.41 | 2 | 12 | 55 | 1130 | 2.8 |
|  | 436 |  | 0.27 | 0.39 |  | 5 | 33 | 390 | 1.0 |
| 24-2 | 0 | 4  | 0.73 | 0.03 |  | 5 | 7 | 120 | 3.6 |
|  | 16 | 4  | 0.75 | 0.10 |  | 2 | 11 | 210 | 2.1 |
|  | 46 | 8  | 0.73 | 0.12 |  | 28 | 7 | 150 | 1.3 |
|  | 76 | 2  | 0.73 | 0.12 |  | 3 | 10 | 180 | 1.5 |
|  | 106 |  | 0.71 | 0.13 |  | 13 | 41 | 170 | 1.3 |
|  | 136 |  | 0.68 | 0.14 |  | 3 | 17 | 380 | 2.6 |
|  | 166 |  | 0.60 | 0.16 | 3 | 3 | 11 | 190 | 1.2 |
|  | 196 |  | 0.54 | 0.29 | 3 | 4 | 15 | 280 | 1.0 |
|  | 226 |  | 0.51 | 0.34 |  | 5 | 12 | 320 | 0.9 |
|  | 256 |  | 0.57 | 0.52 |  | 8 | 40 | 470 | 0.9 |
|  | 286 |  | 0.43 | 0.44 | 2 | 5 | 30 | 350 | 0.8 |
|  | 316 |  | 0.47 | 0.41 | 2 | 6 | 19 | 330 | 0.8 |
|  | 346 |  | 0.56 | 0.46 | 3 | 7 | 20 | 370 | 0.8 |
|  | 376 |  | 0.41 | 0.43 |  | 4 | 10 | 240 | 0.6 |
| F6-3 | 0 | 8  | 0.75 | 0.03 |  | 3 | 30 | 180 | 5.4 |
|  | 16 | 4  | 0.70 | 0.04 |  | 5 | 19 | 770 | 19.8 |
|  | 46 | 3  | 0.76 | 0.18 |  | 4 | 20 | 1040 | 5.9 |
|  | 76 | 3  | 0.77 | 0.08 | 8 | 4 | 14 | 780 | 9.4 |
|  | 106 | 4  | 0.74 | 0.06 |  | 4 | 18 | 740 | 12.1 |
|  | 136 | 3  | 0.72 | 0.06 |  | 2 | 8 | 210 | 3.4 |
|  | 166 | 3  | 0.76 | 0.06 |  | 2 | 8 | 290 | 5.2 |
|  | 196 | 3  | 0.72 | 0.06 |  | 4 | 18 | 380 | 6.8 |
|  | 226 | 3  | 0.73 | 0.07 |  | 2 | 42 | 340 | 5.1 |
|  | 256 | 3  | 0.76 | 0.12 |  | 2 | 18 | 510 | 4.2 |
| C-2 | 0 | 3  | 0.69 | 0.04 |  | 6 | 19 | 170 | 4.4 |
|  | 16 | 1  | 0.71 | 0.04 |  | 6 | 26 |  |  |
|  | 46 | 1  | 0.76 | 0.09 |  | 3 | 15 | 380 | 4.3 |
|  | 76 |   | 0.69 | 0.07 |  | 4 | 20 | 240 | 3.6 |
|  | 106 |  | 0.73 | 0.03 |  | 3 | 14 | 200 | 6.0 |
|  | 136 |  | 0.70 | 0.06 |  |  | 27 | 190 | 3.1 |
|  | 166 |  | 0.71 | 0.05 |  | 5 | 31 | 180 | 3.6 |
|  | 196 |  | 0.73 | 0.07 |  | 6 | 32 | 200 | 3.0 |
|   | 226 |  | 0.73 | 0.07 |   | 3 | 19 | 220 | 3.0 |

##### Table S2. Consumption (−) and production (+) of DIC flux derived from reactive transport simulations. Unit of depth-integrated rates and DIC fluxes from depth are mmol C m−2 yr−1. For calcium and magnesium fluxes from depth, the unit are mmol Ca m−2 yr−1 and mmol Mg m−2 yr−1, respectively.

|  |  |  |  |
| --- | --- | --- | --- |
|  | site A2-2 | site 24-2 | site F6-3 |
| Depth-integrated rate |  |  |  |
| CP-Ca | − 4.51 | − 3.76 | − 2.87 |
| CP-Mg | − 4.51 | − 1.50 | − 0.57 |
| POC degradation | + 40.4 | + 17.0 | + 1.1 |
| AOM | + 851 | + 727 | + 449 |
| OSR | + 33.1 | + 13.0 | + 1.0 |
|  |  |  |  |
| Flux from depth |  |  |  |
| DIC | 358 | 339 | − 27.3 |
| Calcium  | 9.93 | 10.0 | 17.8 |
| Magnesium | 80.6 | 200 | 1.65 |

Table S3. Rate laws used in the modeling.

|  |  |
| --- | --- |
| Rate | Kinectic rate laws |
| Production of DOC |  $R\_{DOC}=K\_{G}∙C\_{org}∙rC∙\frac{K\_{C}}{\left[DIC\right]+\left[CH\_{4}\right]+K\_{C}}$  |
| Methanogenesis | $$R\_{ME}=\frac{1}{2}∙R\_{DOC}∙\frac{K\_{i}SO4}{K\_{i}SO4+\left[SO\_{4}^{2-}\right]}$$ |
| Organioclastic sulfate reduction | $$R\_{OSR}=\frac{1}{2}∙R\_{DOC}∙\frac{\left[SO\_{4}^{2-}\right]}{K\_{half-SO4}+\left[SO\_{4}^{2-}\right]}$$ |
| Anaerobic oxidation of methane | $R\_{AOM}=R\_{AOM}^{MAX}∙\frac{\left[SO\_{4}^{2-}\right]}{K\_{half-SO4}+\left[SO\_{4}^{2-}\right]}∙\frac{\left[CH\_{4}\right]}{K\_{half-CH4}+\left[CH\_{4}\right]}$  |
| Carbonate precipitation | $$R\_{CP}=R\_{CP}^{MAX}∙exp\left(-0.5∙\frac{x\_{cp}-x}{s\_{cp}}\right)$$ |

Table S4. Rate expressions applied in the differential equations

|  |  |
| --- | --- |
| Species | Rates |
| DOC | $R\_{DOC-f}=R\_{DOC}-R\_{ME}-R\_{OSR}$  |
| TA | $$R\_{TA}=R\_{AOM}+R\_{OSR}+R\_{ME}-R\_{CP-Mg}-R\_{CP-Ca}$$ |
| Magnesium | $$R\_{Mg}=-R\_{CP-Mg}$$ |
| Calcium | $R\_{Ca}=-R\_{CP-Ca}$  |
| Bromide | $$R\_{Br}=+r\_{Br}∙R\_{DOC}$$ |
| Ammonium | $$R\_{NH4}=+14/12∙{N\_{s}}/{C\_{s}}∙rN/rC∙R\_{DOC}$$ |

##### Table S5. Parameters and boundary conditions applied in numerical modeling.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| parameter | symbol | unit | A2-2 | 24-2 | F6-3 | reference |
| temperature |  | oC | 10.5 |  |  | Chen et al., 2020 |
| diffusion coefficient of total alkalinity | DiTA | m2 yr-1 | 0.0251 |  |  | Wallmann et al., 2006 |
| diffusion coefficient of calsium | DiCa | m2 yr-1 | 0.0173 |  |  | Boudreau, 1997 |
| diffusion coefficient of magnesium | DiMg | m2 yr-1 | 0.0157 |  |  | Boudreau, 1997 |
| diffusion coefficient of DOC | DiDOC | m2 yr-1 | 0.0051 |  |  | Komada et al., 2013 |
| diffusion coefficient of bromide | DiBr | m2 yr-1 | 0.0463 |  |  | Boudreau, 1997 |
| diffusion coefficient of ammonium | DiNH4 | m2 yr-1 | 0.0441 |  |  | Boudreau, 1997 |
| Length of model column  |  | m | 4.4 | 3.8 | 2.6 | Chen et al., 2020 |
| porosity at sediment surface |  |  | 0.50 | 0.50 | 0.42 | Chen et al., 2020 |
| porosity at end of coulmn |  |  | 0.41 | 0.40 | 0.38 | Chen et al., 2020 |
| empirical coefficient for porosity fitting |  | m-1 | 2 | 2 | 1 | Chen et al., 2020 |
| total organic carbon (TOC) | C-org | wt % | 0.45 | 0.45 | 0.45 | Chen et al., 2020 |
| rate constant of degradation of organic carbon | KG | yr-1 | 10-6 | 10-6 | 10-6 | Vanneste et al., 2011 |
| velocity of upward fluid | u0 | m yr-1 | 0.02 | 0.01 | 0.00 | Chen et al., 2020 |
| depth of bubble irrigation | Lirr | m | 2.8 | 1.5 | 2.3 | Chen et al., 2020 |
| Irrigation coefficient ( alpha0, yr -1)  |  | yr-1 | 0.55 | 0.25 | 0.20 | Chen et al., 2020 |
| Irrigation coefficient ( alpha1, cm) |  | m | 0.1 | 0.15 | 0.05 | Chen et al., 2020 |
| rate constant of AOM | KAOM | mM-1 yr-1 | 2 | 2 | 2 | Chen et al., 2020 |
| half saturation constant of sulfate | Khalf-SR |  | 0.5 | 0.5 | 0.5 | Nauhaus et al., 2002; Vavilin, 2013; Wegener and Boetius, 2009 |
| half saturation constant of methane | Khalf-AOM |  | 5 | 5 | 5 |
| Constant for inhibition of POC degradation | KC |  | 35 | 10 | 50 | Wallmann et al., 2006 |
| The maximum rate of CP  | $R\_{CP}^{MAX}$-Ca | mM yr-1 | 0.006 | 0.005 | 0.004 |  |
| The maximum rate of CP | $R\_{CP}^{MAX}$-Mg | mM yr-1 | 0.006 | 0.002 | 0.0008 |  |
| The sediment depth of $R\_{CP}^{MAX}$ | xcp | m | 2.7 | 1.4 | 2.1 |  |
| The width of the Gaussian function for the depth distribution of CP | scp | m | 0.3 | 0.3 | 0.3 |  |
| Ca concentration at upper boundary | CaU | mM | 9 | 8.5 | 10 | Chen et al., 2020 |
| Ca concentration at lower boundary | CaL | mM | 1 | 1 | 2 | Chen et al., 2020 |
| Mg concentration at upper boundary | MgU | mM | 49 | 49 | 47.5 | Chen et al., 2020 |
| Mg concentration at lower boundary | MgL | mM | 5 | 20 | 46 | Chen et al., 2020 |
| TA concentration at upper boundary | TAU | mM | 2.7 | 2.7 | 2.67 | Chen et al., 2020 |
| TA concentration at lower boundary | TAL | mM | 36 | 34 | 26 | Chen et al., 2020 |
| DOC concentration at upper boundary | DOCU | mM | 0.25 | 0.15 | 0.15 |  |
| DOC concentration at lower boundary | DOCL | mM | 0.4 | 0.4 | 0.5 |  |
| Bromide concentration at upper boundary | BrU | mM | 0.70 | 0.73 | 0.75 |  |
| Bromide concentration at lower boundary | BrL | mM | 0.27 | 0.41 | 0.76 |  |
| Ammonium concentration at upper boundary | NH4U | mM | 0.03 | 0.03 | 0.03 |  |
| Ammonium concentration at lower boundary | NH4L | mM | 0.40 | 0.43 | 0.12 |  |
| ratio of TOC to TN in sediment | Cs/Ns |  | 5.58 | 5.58 | 5.58 | Su, 2015 |

## Supplementary Figures



Figure S1. *ex-situ* pH values of porewater throughout sediment columns at all sites.

# References

Boudreau, Bernard P. *Diagenetic Models and Their Implementation.* Vol. 505: Springer Berlin, 1997.

Burdige, David J, Tomoko Komada, Cédric Magen, and Jeffrey P Chanton. "Carbon Cycling in Santa Barbara Basin Sediments: A Modeling Study." *Journal of Marine Research* 74, no. 3 (2016): 133-59.

Komada, Tomoko, David J Burdige, Sabrina M Crispo, Ellen RM Druffel, Sheila Griffin, Leah Johnson, and Diemmi Le. "Dissolved Organic Carbon Dynamics in Anaerobic Sediments of the Santa Monica Basin." *Geochimica et Cosmochimica Acta* 110 (2013): 253-73.

Nauhaus, Katja, Antje Boetius, Martin Krüger, and Friedrich Widdel. "In Vitro Demonstration of Anaerobic Oxidation of Methane Coupled to Sulphate Reduction in Sediment from a Marine Gas Hydrate Area." *Environmental microbiology* 4, no. 5 (2002): 296-305.

Vanneste, H., B. A. Kelly-Gerreyn, D. P. Connelly, R. H. James, M. Haeckel, R. E. Fisher, K. Heeschen, and R. A. Mills. "Spatial Variation in Fluid Flow and Geochemical Fluxes across the Sediment-Seawater Interface at the Carlos Ribeiro Mud Volcano (Gulf of Cadiz)." [In English]. Article. *Geochimica Et Cosmochimica Acta* 75, no. 4 (Feb 2011): 1124-44. <https://doi.org/10.1016/j.gca.2010.11.017>. <Go to ISI>://WOS:000286960400010.

Vavilin, VA. "Estimating Changes of Isotopic Fractionation Based on Chemical Kinetics and Microbial Dynamics During Anaerobic Methane Oxidation: Apparent Zero-and First-Order Kinetics at High and Low Initial Methane Concentrations." *Antonie van Leeuwenhoek* 103, no. 2 (2013): 375-83.

Wallmann, K., Aloisi, G., Haeckel, M., Obzhirov, A., Pavlova, G., Tishchenko, P. "Kinetics of Organic Matter Degradation, Microbial Methane Generation, and Gas Hydrate Formation in Anoxic Marine Sediments." *Geochimica Et Cosmochimica Acta* 70, no. 15 (2006): 3905-27. <https://doi.org/10.1016/j.gca.2006.06.003>. <Go to ISI>://WOS:000239765800010.

Wegener, Gunter, and Antje Boetius. "An Experimental Study on Short-Term Changes in the Anaerobic Oxidation of Methane in Response to Varying Methane and Sulfate Fluxes." *Biogeosciences* 6, no. 5 (2009): 867-76.