|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Depth** | **210Pbxs (mBq/g)** | **137Cs (mBq/g)** |
| *Core 1* |  |  |  |  |  |  |  |
|  | 0.5 | 101 | ± | 31 | -2 | ± | 3 |
|  | 10.5 | 131 | ± | 12 | 3 | ± | 1 |
|  | 21.5 | 88 | ± | 5 | 3 | ± | 0 |
|  | 30.5 | 58 | ± | 11 | 4 | ± | 1 |
| *Core 2* |  |  |  |  |  |  |  |
|  | 1.5 | 90 | ± | 6 | 3 | ± | 0 |
|  | 10.5 | 80 | ± | 7 | 2 | ± | 1 |
|  | 20.5 | 58 | ± | 4 | 3 | ± | 0 |
|  | 35.5 | 32 | ± | 4 | 1 | ± | 0 |
| *Core 3* |  |  |  |  |  |  |  |
|  | 0.5 | 127 | ± | 15 | 0 | ± | 1 |
|  | 10.5 | 110 | ± | 15 | 1 | ± | 1 |
|  | 20.5 | 68 | ± | 14 | 1 | ± | 1 |

**Table 1.** 210Pbxs and 137Cs activities in sediments.

**Fig 1.** Depth profile of porosity in sediments.

**Fig 2.** Depth profiles of chloride in sediments.

**1. Steady State model**

In the steady state model, we first fit the sulfate profiles shallower than 20 cm from Core 1&2 with a 2-order polynomial trend. Sulfate concentration below 20 cm was assumed to be constant (0.28 mM). The 34S of sulfate was fitted in the same fashion. After deriving 34S/32S ratios from the fitted trend of 34S record (assuming the Canyon Diablo Troilite standard has the 34S to 32S ratio of 0.0450045), we calculated concentrations of 32S total sulfate concentration. We set 16 grids for the 40-cm sediment column. For each grid, we calculated the input flux (with Fick’s first law) for both 34S and 32S of sulfate from the grid above the target grid and output fluxes towards the grid below. The net SRR at each grid is the difference between the input and out fluxes. Porosity was assumed to be 0.9 and diffusion coefficient for sulfate as 0.0337 m2/yr (Boudreau, 1997).

After estimating the net SRR for 32S (i.e., sum of 32RAOM and 32ROSR), we assumed the rate constants for OSR and AOM-SR differently in the three modes we tested. In the “constant-k” mode, we assumed all SR can be attributed to OSR until 17.5 cmbsf (i.e., no AOM-SR until that level). AOM-SR only happens in the grid of 20cm, where most sulfate is consumed. Rate constants for OSR with respect to 32S were assumed to be “1” (a unitless scaling parameter). AOM-SR rates (32RAOM) for 32S were calculated from the difference of net SRR and OSR rates; rate constants (32kAOM) were estimated following the expression:

32kAOM = 32RAOM / 32SO4

which is 0 m/yr until 17.5 cm and 1.35 m/yr at 20 cm. The fractionations () of OSR and AOM-SR were estimated in a rate-dependent fashion (Dale et al., 2009):

i = max - mSR \* Ri

Where i = AOM or OSR and max is the theoretical maximum fractionation, R is the net rate of OSR or AOM-SR (i.e., 32R + 34R) and mSR determines the variability of fractionation with rates. We used 78‰ for max and 1.5 yr/mM for mSR following the suggestions from Dale et al. (2009) and Farquhar et al. (2003). The rate constants, 34kAOM and 34kOSR, can then be estimated following:

32ki / 34ki = I

i = 1+i/1000

where i = AOM or OSR and  is the fractionation factors for particular pathways. Once we estimated 34RAOM and 34ROSR following the similar fashion of Eq., we can calculated the concentration of 34SO4 as based on these rates and fluxes from grid above and below. 34S was then estimated from the concentration of 32SO4 and 34SO4, and compared with the observed values.

For the “variable-k” mode, all the calculation is the same as above except that we assumed 32kOSR decreases by 0.05 for each grid deeper “. 32kOSR decreases follow the exact fashion with sediment age as proposed by Middelburg (1989) in the “Middelburg mode”. The age of the sediment was estimated from the sedimentation rate (7.6 m/yr).

The major uncertainties of this calculation lay within the values assigned for Eq. and the age dependency of kOSR. It is therefore more important to pay attention to the structure of the profiles than the absolute values. All models can reproduce the structure of our measured 34S profiles.



**Fig 3.** Fractionations applied to AOM-SR and OSR.

**2. Non-steady state model**

For our non-steady state model, we coupled CrunchFlow (Steefel, 2009) with a customized MATLAB code to simulate reactions, diffusion, and sediment burial. This modeling strategy has been successfully applied by Hong et al. (2016). More details were provided in the aforementioned paper. In this model, we simulation the fluid evolution for a 20-cm sediment column with 200 grids (0.1 cm thick for each grid) over a time course of 25 years. CrunchFlow evaluated diffusion and reactions for each 2.5-year time slice; our MATLAB code then simulate the burial of both pore fluid and sediments for this 2.5 years. We assumed both liquid and solid phases were buried for a same rate; in other words, compactional fluid advection is excluded in the current model. We included 8 primary chemical species (sulfate, methane, hydrogen sulfide, ammonium, phosphate, chloride, bicarbonate, and sodium) and another 8 secondary chemical species (CO2, CO32-, H3PO4, H2PO4-,PO43-, H2S, and S2-) to account for effects from ionic strength, charge balance, and pH in the pore fluid. See Hong et al. (2014) for the detail reactions of the secondary species. The secondary species responses not only to the primary reactions we assigned (AOM-SR and OSR in this case) but also any redistribution of primary species due to diffusion and burial. OSR was formulated as *Monod-type* rate expression with one *Monod* term:





where *Am* (=1) and *km* are the surface area and kinetic constant. *Ea*, *R*, and *T* are the activation energy, ideal gas constant, and temperature. *ain* is the activity product of solutes in the reaction with their stoichiometry (*n*) as exponents.  determines the direction of reaction where *Q* is the ion activity product and *Keq* is the equilibrium constant. As OSR is a kinetic-driven reaction, we arbitrarily assigned a *Keq* to ensure the reaction always in a forward direction. **is the theoretical maximum rate that was assigned based on our assumption of organic matter reactivity (Table S2). *Khalf* is the half saturation constant (=100 µM; Wegener and Boetius, 2009), and *CSO4* is the concentration of sulfate.

AOM-SR was formulated as *Monod-type* reactions with two *Monod* terms:



where *C* is the concentration of electron donors or acceptors and *Q* is the ion activity product.

and were set to be 500 µM (Wegener and Boetius, 2009) and 5 mM (Nauhaus et al., 2002; Vavilin, 2012), respectively. *,* was obtained from fitting curves to our data.

The four scenarios we assigned in this work are different with respect to the reactivity of organic matter, modes of sedimentation, initial conditions, and the time scale focused. Table S2 listed the different setup for the four scenarios.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Scenario 1** | **Scenario 2** | **Scenario 3** | **Scenario 4** |
| Top boundary condition | Topmost measured values | Topmost measured values | Topmost measured values | Topmost measured values |
| Bottom boundary condition | No flux boundary for sulfate | No flux boundary for sulfate | No flux boundary for sulfate | No flux boundary for sulfate |
| Initial condition | Same as top boundary | Same as top boundary | The results from scenario 2 | The results from scenario 2 |
| Temporal scale (yr) | 25 | 25 | 12.5  | 0.25 |
| Depth scale (cm) | 20  | 20 | 20 | 20 |
| Theoretical maximum OSR rate (mol.kg (H2O) -1.yr-1) | 10-6 | 10-6.5 | 10-6 for the first 10 cm and 0 below | 10-4.9 for the first 5 cm and 0 below |
| Sedimentation rate | Constant sedimentation | Constant sedimentation | Constant sedimentation | No sedimentation except for the instantaneous input of the first 5 cm layer |

**Table 2**. Different conditions assigned for the four scenarios.

**References**

 Boudreau, B.P., 1997. Diagenetic models and their implementation: modelling transport and reactions in aquatic sediments. Springer.

Dale, A.W., Brüchert, V., Alperin, M., Regnier, P., 2009. An integrated sulfur isotope model for Namibian shelf sediments. Geochim. Cosmochim. Acta 73, 1924–1944. doi:10.1016/j.gca.2008.12.015

Farquhar, J., Johnston, D.T., Wing, B.A., Habicht, K.S., Canfield, D.E., Airieau, S., Thiemens, M.H., 2003. Multiple sulphur isotopic interpretations of biosynthetic pathways: implications for biological signatures in the sulphur isotope record. Geobiology 1, 27–36. doi:10.1046/j.1472-4669.2003.00007.x

Hong, W.-L., Sauer, S., Panieri, G., Ambrose, W.G., James, R.H., Plaza-Faverola, A., Schneider, A., 2016. Removal of methane through hydrological, microbial, and geochemical processes in the shallow sediments of pockmarks along eastern Vestnesa Ridge (Svalbard). Limnol. Oceanogr. n/a-n/a. doi:10.1002/lno.10299

Hong, W.-L., Torres, M.E., Kim, J.-H., Choi, J., Bahk, J.-J., 2014. Towards quantifying the reaction network around the sulfate–methane-transition-zone in the Ulleung Basin, East Sea, with a kinetic modeling approach. Geochim. Cosmochim. Acta 140, 127–141. doi:10.1016/j.gca.2014.05.032

Middelburg, J.J., 1989. A simple rate model for organic matter decomposition in marine sediments. Geochim. Cosmochim. Acta 53, 1577–1581. doi:10.1016/0016-7037(89)90239-1

Nauhaus, K., Boetius, A., Krüger, M., Widdel, F., 2002. In vitro demonstration of anaerobic oxidation of methane coupled to sulphate reduction in sediment from a marine gas hydrate area. Environ. Microbiol. 4, 296–305. doi:10.1046/j.1462-2920.2002.00299.x

Steefel, C.I., 2009. CrunchFlow. Softw. Model. Multicomponent React. Flow Transp. User’s Man. Lawrence Berkeley Natl. Lab. Berkeley USA.

Vavilin, V.A., 2012. 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, 375–383. doi:10.1007/s10482-012-9818-8

Wegener, G., Boetius, A., 2009. An experimental study on short-term changes in the anaerobic oxidation of methane in response to varying methane and sulfate fluxes. Biogeosciences 6, 867–876. doi:10.5194/bg-6-867-2009