geosciences

Supplementary Materials

S1. Methane Flux and the Sulfate Methane Transition Zone (SMTZ)

In order to further validate our assumption that the HASR represents methane gas concentrations above the saturation level, we have modeled the sulfate methane transition zone (SMTZ) in the study area. The SMTZ is modeled using the observed cutoff of the HASR picks at 25 mbsf (Figure 9). The SMTZ is a well recorded and studied phenomena [1–7], induced by consumption of sulfate in sediments by one of the fowling reactions:

$$(SO_4^{2-} + 2CH_2O \Rightarrow H_2S + 2HCO^{3-})$$

$$(SO_4^{2-} + CH_4 \Rightarrow HS^- + HCO_3^- + H_2O)$$

The former is mediated by sulfate-reducing microbes [8,9], and the latter occurs under anaerobic conditions where methane is oxygenated by sulfate ions. This process requires a constant supply of methane to the zone [10,11].

The model relays on the same P-T-S thermodynamic parameters that were used for modeling the GHSZ and is calculating the SMTZ depth below the seafloor based on the following main assumptions: (1) the seafloor represents one endmember in which the sulfate concentration is assumed to be equal to that of seawater (30 mmol) (e.g. [4,12,13]); (2) the interstitial pore water at the level of the HASR are saturated with respect to methane, representing the opposite endmember (e.g. [7,14]); (3) both the methane and sulfate concentrations are reduced to zero at the SMTZ; (4) a steady flow of methane gas throughout the modeled sediment column; (5) no crystallization of sulfate occurs and the amount of in situ production of methane in the sediment is negligible. This notion is debatable, mainly due to lack of observational data, thus limiting this model to constituting a first order approximation.

Methane saturation values at the HASR top cutoff level are calculated by "Methanesolubility" Matlab function (Appendix. 3) based in the work of [15,16]. Consequently, the sulfate and methane fluxes can be written as follows:

Sulfate flux

$$J_{SO4} = -Ds_{(SO4)} \times (SO_4(0) - SO_4\,(F)) / (0-X) = -Ds_{(SO4)} \times SO_4(0) / X$$

Methane flux

$$J_{CH4} = -Ds_{(CH4)} \times (CH_4\,(0) - CH_4(F) / (X-F) = -Ds_{(CH4)} \times CH_4(F) / (F-X)$$

These two equations should be equal in order to create a steady state at the SMTZ depth, resulting in the fowling equation:

$$X = (Ds_{(SO4)} \times SO_4(0) \times F) / (Ds_{(SO4)} \times SO_4(0) + Ds_{(CH4)} \times CH_4(F))$$

where: X= depth of the MSTZ m bellow the sea floor, $Ds_{(SO4)}$ = 5.6e-6 cm^2/s diffusion coefficient of sulfate [17], $Ds_{(CH4)}$ = 8.7e-6 cm^2/s diffusion coefficient of methane [17], F= depth of the HASR, estimate as 25 mbsf, $CH_4(F)$ = methane saturation concentration at the depth of the HASR, $SO_4(0)$ = sulfate concentration at the water-sediment interface.

Our model predicts the occurrence of an SMTZ at a sediment depth of 4.5 m. The calculated upward methane flux equal to the downward sulfate flux of 200 mmol×m^{-2}/a.

S2. Manual Picking of the HASR

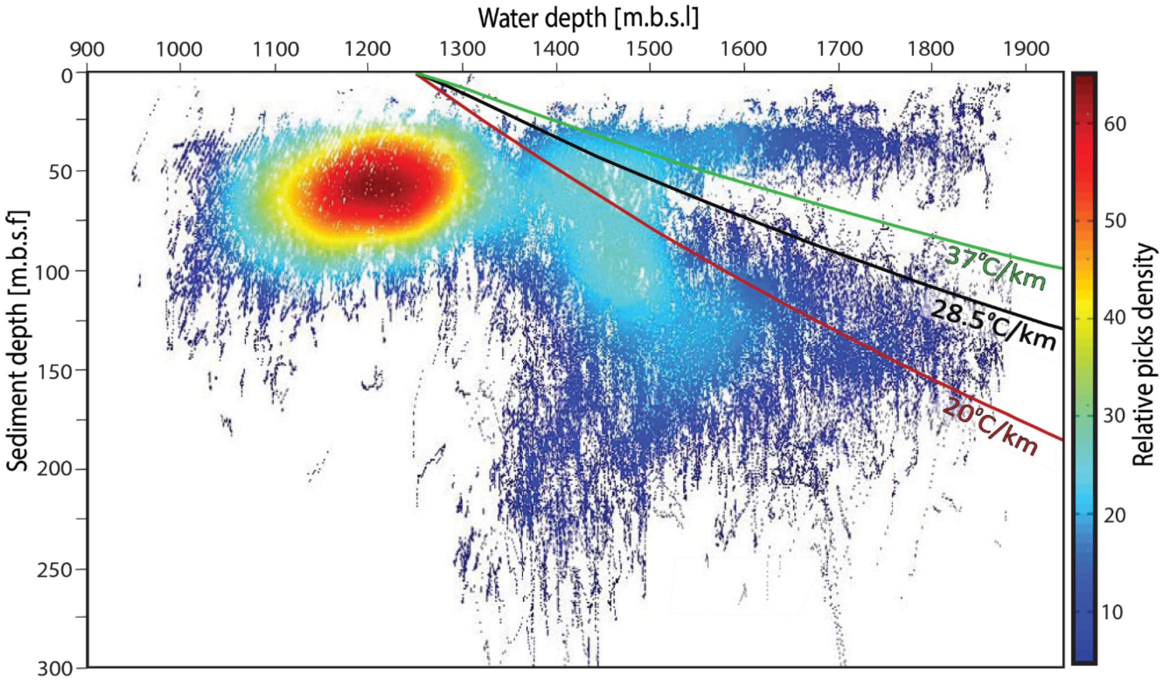

Figure S1. The distribution of the manually picked HASR picks with respect to the seafloor water depth and the sediments depth below the seafloor. The color scale (right) represents the relative density of picks. Overlain curves are the base GHSZ models for geothermal gradients of 20° C/km (red), 28.5° C/km (black) and 37° C/km (green). The Shallow and Deepening HASR clusters are evident as distinct trends of high picks-distributions.

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