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Quarterly Research Performance Progress Report
(Period ending 06/30/2013)

Application of Crunch-Flow Routines to Constrain Present and Past Carbon Fluxes at Gas-Hydrate Bearing Sites
Project Period: October 1, 2012 – September 30, 2013

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EXECUTIVE SUMMARY

In November 2012, Oregon State University initiated the project entitled: **Application of Crunch-Flow routines to constrain present and past carbon fluxes at gas-hydrate bearing sites.** This project aims to develop modeling modules that include all important biogeochemical processes that need to be considered in methane-rich marine sediment systems. These modules will be applied to data collected from several DOE-supported drilling expeditions (e.g., Cascadia margin in US, Ulleung Basin in south Korea) to quantify the dynamics of methane at present and in the past.

For the second quarter (April to June), we have developed a kinetic model to simulate the network of interconnected reactions that occur at the depth of the sulfate-methane transition zone (SMTZ), and applied the model to the 8 sites drilled in Ulleung Basin during UBGH2 in 2010. These 8 sites include 5 non-chimney sites and 3 chimney sites. We show that organic matter degradation by sulfate reduction and methanogenesis plays important in non-chimney sites, while a strong methane flux from deep reservoirs (e.g., gas hydrate, free gas, etc) plays a key role in the chimney sites, in which most of the sulfate is consumed by anaerobic oxidation of methane (AOM). The dynamic response of sulfate reduction and methanogenesis to changes in methane flux has a profound effect on the quantity and pathway of organic matter degradation, methane generation and overall carbon budgets in continental margins, which are a key component of global gas hydrate assessment efforts.

PROGRESS, RESULTS, AND DISCUSSION

We developed a kinetic model using CrunchFlow, a FORTRAN routine developed by Steefel (2009). It includes diffusion, advection and reactive terms and is internally linked to a large thermodynamic and kinetic database. To constrain the carbon and sulfur cycling in the sediments above and just below the SMTZ, we included 20 reactions listed in Appendix1 with the 5 reactions most focused in Figure 1, and a reaction network illustrated in Figure 2. The fundamental building blocks of the model include 15 primary species, 10 secondary species, 5 gases, and 5 minerals, which are listed in Appendix 2.

We applied this model to the 8 sites drilled in during the second Ulleung Basing Gas Hydrate Expedition (UBGH2), which include 5 sites thought to be controlled by diffusion processes and 3 sites that targeted acoustic blanking chimneys thought to represent advective transport of methane gas. In non chimney sites the depth of the SMTZ usually ranges from 6.2-8 mbsf, in contrast in the chimney sites the SMTZ occurs at much shallower depths, typically 1.2-2 mbfs. Therefore, for the non-chimney sites we used a 20 meters tick sediment column, whereas only 5 meters of sediment were considered at the three chimney sites. We ran the simulation for a time period equivalent to that needed to accumulate the modeled sediment column (400 kyr). Although steady state is not assumed, such time span is long enough for all dissolved and solid species to reach steady state.

Our model can successfully reproduce the concentration and isotopic profiles observed at these 8 drilled sites. As a result, the reaction rates and solute fluxes be quantified, and demonstrate the relative significance of each reaction in cycling organic carbon at the SMTZ. Here we use one site from each non-chimney (Figure 3 for UBGH2-1-1) and chimney sites (Figure 4 for UBGH2-3) to demonstrate the outputs of our model, which show a striking difference in the biogeochemical processes that control the biogeochemical processes in these two contrasting settings.

In the non-chimney sites, most (49-85%) of the organic matter is degraded through sulfate reduction (POCSR, reaction 1 in Figure 1), and only a small fraction (15-51%) is available for microbial methanogenesis. Sulfate reduction of organic carbon is also responsible for most (37-70%) of the DIC production at this site. Here, AOM (Reaction 1 in Figure 1) is fueled by methane that originates from three different sources: about 26-51% comes from in-situ organic matter degradation via methanogenesis (ME; reaction 4 in Figure 1); another 19-32% originates via CO_2 reduction within an internal cycle of carbon between pools of DIC and methane below SMTZ (CR, reaction 3 in Figure 1); and the remaining is supplied to the reaction zone from outside the modeled sediment domain, i.e. and external methane source (Figure 1C).

In contrast, at the chimney sites, more than 70% of the AOM is fueled by an external methane flux, and the remaining ~20-30% is supported by methane produced from CO_2 reduction and organic matter degradation (<10% CR and 11-21% ME; Figure 2C). The high methane flux in these settings also acts to shoal the SMTZ, in effect shrinking the sulfate reduction zone, and thus most of the organic matter escapes oxidation by sulfate and gets buried into the methanogenesis zone. Consequently, most (>65%) of the organic matter reaching the seafloor is available to the methanogens, and their enhanced activity is evidenced by the isotopically heavy DIC and methane observed at the chimney sites (Figure 2B). Abundant methane is produced from the labile organic matter, which makes the SMTZ even shallower and further enhances methane production.

We are now preparing a manuscript to be submitted to Geochimica et Cosmochimica Acta. A draft of this document should be ready to circulate among the co-authors and seek NETL approval for publication by the end of June.

Task	Subtasks	
TASK 1 SMTZ biogeochemical cycling	1.1 Adapt CrunchFlow code to accept (and simulate) carbon isotope data.	Done
	1.2 Set up the model framework: discretization of spatial and temporal modeling domain, species (primary, secondary, gas, and minerals) considered, and thermodynamic and kinetic database entries.	Done
	1.3 Verify and test model parameters with field observations.	Done
	1.4 Compare the results from CrunchFlow with our previous box model and re-adjust the model if necessary.	Done
	1.5 Run sensitivity tests to evaluate significance of environmental variables in the of the resulting fraction of contributions from each carbon cycling reactions, and effects on the SMTZ depth	Done
	1.6 Preparing a manuscript to document our kinetic model	In progress

COST STATUS

MILESTONE STATUS

Title:	Carbon cycling around the present SMTZ
Planned Date:	Mar 1, 2013
Verification Method:	Comparison with our previous box model and similar models published.

Status: Model completed, preparing manuscript for publication

ACCOMPLISHMENTS

A CrunchFlow modeling routine was developed to simulate a complex and interdependednt reaction network at the SMTZ. This model has been applied to the data from Ulleung Basin and provides useful insights on the overall carbon cycle and methane generation in marginal basins.

PROBLEMS OR DELAYS

None

PRODUCTS

→ This progress report
→ A kinetic model that is ready to apply to other regions to describe the biogeochemical cycling around SMTZ.

Figure 1

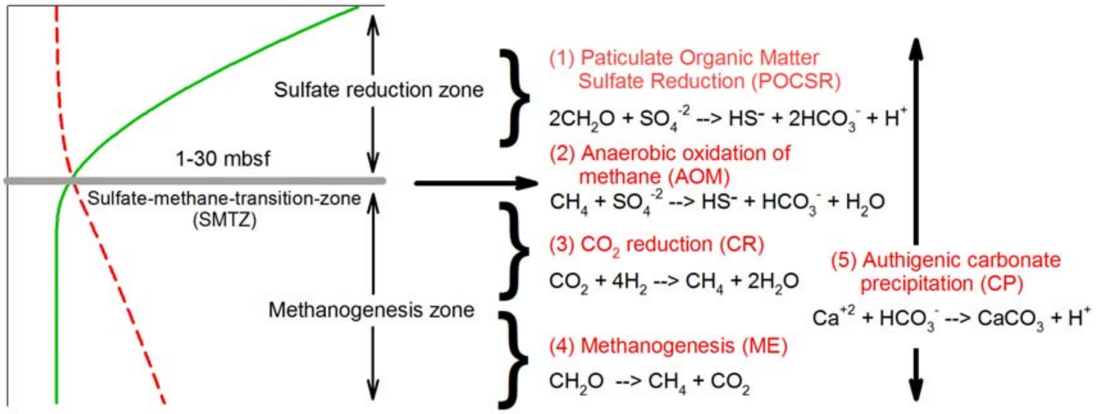
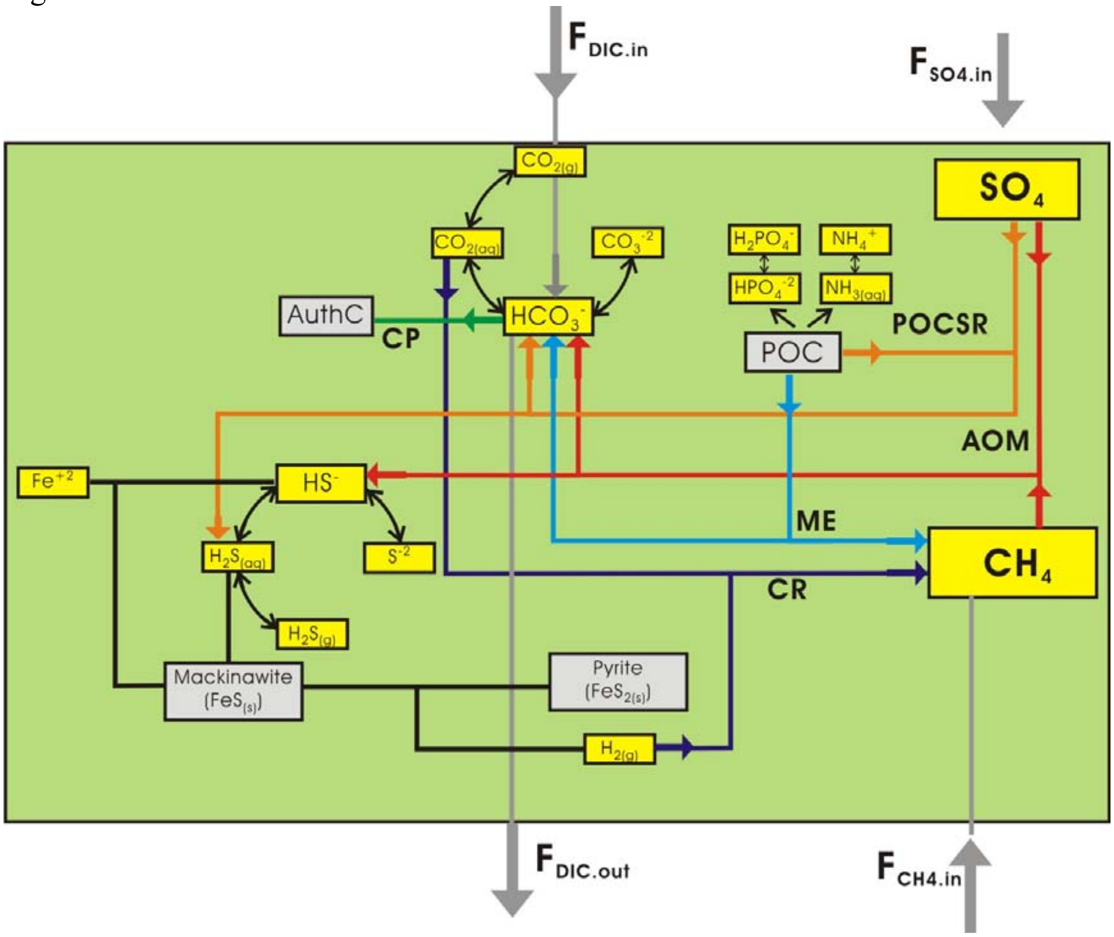

Sulfate reduction zone
1-30 mbsf
Sulfate-methane-transition-zone (SMTZ)
Methanogenesis zone
(1) Paticulate Organic Matter Sulfate Reduction (POCSR)
$2CH_2O + SO_4^{-2} \dashrightarrow HS^- + 2HCO_3^- + H^+$
(2) Anaerobic oxidation of methane (AOM)
$CH_4 + SO_4^{-2} \dashrightarrow HS^- + HCO_3^- + H_2O$
(3) CO_2 reduction (CR)
$CO_2 + 4H_2 \dashrightarrow CH_4 + 2H_2O$
(4) Methanogenesis (ME)
$CH_2O \dashrightarrow CH_4 + CO_2$
(5) Authigenic carbonate precipitation (CP)
$Ca^{+2} + HCO_3^- \dashrightarrow CaCO_3 + H^+$

Figure 2



$F_{DIC.in}$
$F_{SO4.in}$
$CO_{2(g)}$
SO_4
$CO_{2(aq)}$
CO_3^{-2}
$H_2PO_4^-$
NH_4^+
HPO_4^{-2}
$NH_{3(aq)}$
AuthC
HCO_3^-
CP
POCSR
POC
AOM
Fe^{+2}
HS^-
ME
$H_2S_{(aq)}$
S^{-2}
CH_4
CR
$H_2S_{(g)}$
Mackinawite
$(FeS_{(s)})$
Pyrite
$(FeS_{2(s)})$
$H_{2(g)}$
$F_{DIC.out}$
$F_{CH4.in}$

Figure 1: (A) & (B) Reaction rates of all carbon-related reactions for site UBGH2-1_1. (C) Depth-integrated reaction rates in terms of methane production and consumption. (D) Isotope and concentration profiles.

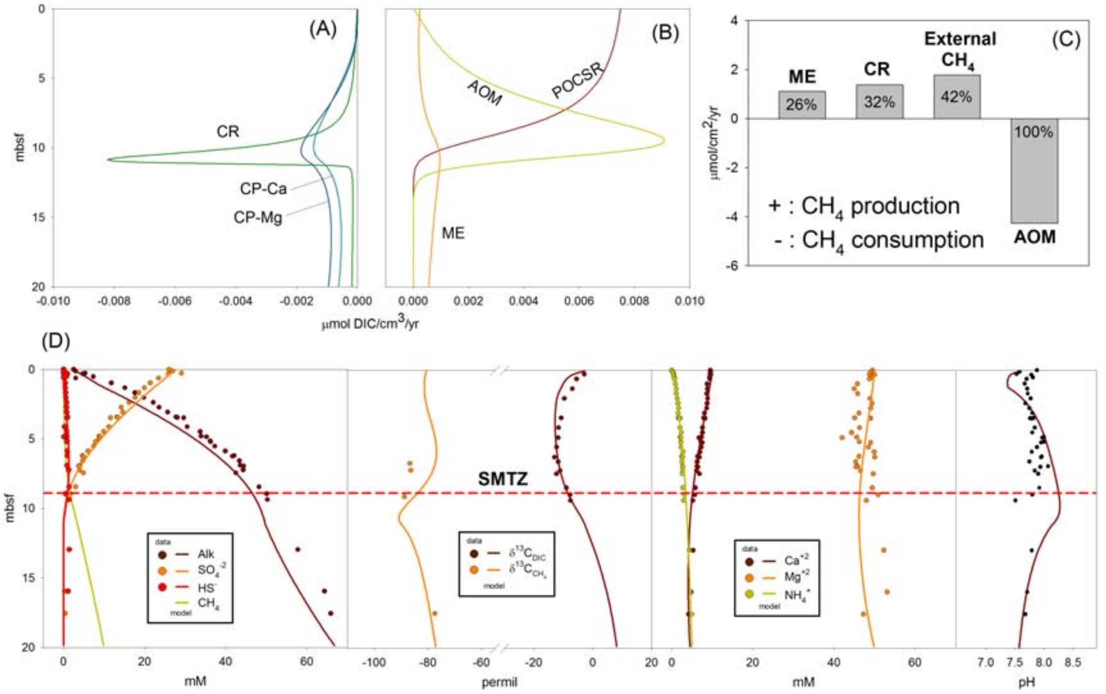
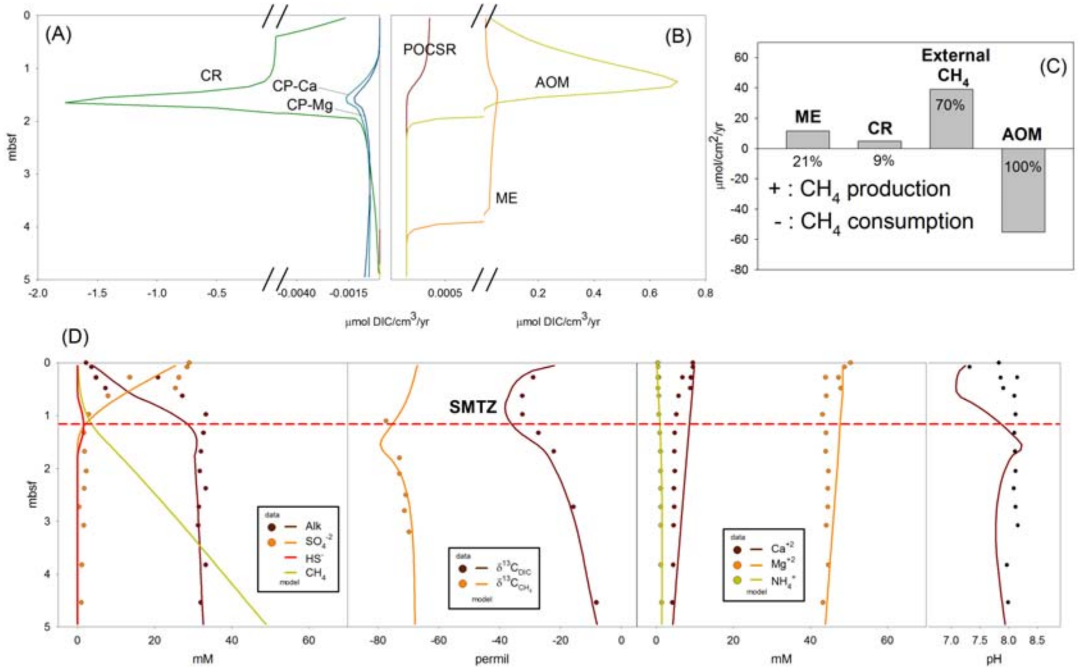


Figure 2: (A) & (B) Reaction rates of all carbon-related reactions for site UBGH2-3. (C) Depth-integrated reaction rates in terms of methane production and consumption. (D) Isotope and concentration profiles.



Appendix 1

Homogeneous reactions	
Acid-base	$H_2O+{}^{12/13}CO_2 \rightarrow H^{12/13}CO_3^-+H^+$
	$H^{12/13}CO_3^- \rightarrow {}^{12/13}CO_3^{-2}+H^+$
	$NH_4^+ \rightarrow NH_{3(aq)}+H^+$
	$H_3PO_4 \rightarrow H_2PO_4^-$
	$H_2PO_4^- \rightarrow HPO_4^{-2}$
	$HPO_4^{-2} \rightarrow PO_4^{-3}$
	$H_2S_{(aq)} \rightarrow HS^-+H^+$
	$HS^- \rightarrow S^{-2}+H^+$
	$FeS_{(aq)} + H^+ \rightarrow HS^- + Fe^{+2}$
Gas-dissolvent	${}^{12/13}CH_{4(g)} \rightarrow {}^{12/13}CH_{4(aq)}$
	${}^{12/13}CO_{2(g)} \rightarrow {}^{12/13}CO_{2(aq)}$
	$H_2S_{(g)} \rightarrow H_2S_{(aq)}$
Aquatic redox	AOM: ${}^{12/13}CH_{4(aq)}+SO_4^{-2} \rightarrow H^{12/13}CO_3^-+HS^-+H_2O$
	CR: $H^{12/13}CO_3^-+ H^+ +4H_{2(aq)} \rightarrow {}^{12/13}CH_{4(aq)}+3H_2O$
Heterogeneous reactions	
Calcite	$(Ca\ ,Mg)\ CO_{3(s)}+H^+ \rightarrow (Mg^{+2}\ ,Ca^{+2})+\ (1\text{-}a)H^{12}CO_3^-+ aH^{13}CO_3^-$
CH2O-SO4	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{-2} +14H^+ \rightarrow$ $53H_2S + (106\text{-}b)H^{12}CO_3^- + bH^{13}CO_3^-+ 16NH_4^+ + HPO_4^{-2}$
CH2O-ME	$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 14H_2O$ $\rightarrow (53\text{-}c)^{12}CH_4 + c^{13}CH_4 +(39\text{-}d)^{12}CO_2 +d^{13}CO_2 +(14\text{-}e)H^{12}CO_3^- + eH^{13}CO_3^- +16NH_4^+ + HPO_4^{-2}$
Pyrite ($FeS_{2(s)}$)	Pyrite + $H_{2(aq)} \rightarrow$ Mackinawite + $H_2S_{(aq)}$
Mackinawite ($FeS_{(s)}$)	Mackinawite + $H^+ \rightarrow Fe^{+2} + HS^-$
Ammonium adsorption	$NH_4^+ + MX \rightleftharpoons NH_4X + M^+$

Appendix 2

Primary Species	*Secondary Species*	*Gases*	*Minerals*
$H^{12}CO_3^-$	$^{12}CO_{2(aq)}$	$^{12}CO_{2(g)}$	Calcite-Ca
$H^{13}CO_3^-$	$^{13}CO_{2(aq)}$	$^{13}CO_{2(g)}$	Calcite-Mg
$^{12}CH_{4(aq)}$	$^{12}CO_3^{-2}$	$H_2S_{(g)}$	CH_2O
$^{13}CH_{4(aq)}$	$^{13}CO_3^{-2}$	$^{12}CH_{4(g)}$	Pyrite
NH_4^+	$NH_{3(aq)}$	$^{13}CH_{4(g)}$	Mackinawite
HPO_4^{-2}	$H_3PO_{3(aq)}$		
HS^-	$H_2PO_4^-$		
SO_4^{-2}	PO_4^{-3}		
Fe^{+2}	$H_2S_{(aq)}$		
H^+	S^{-2}		
$H_{2(aq)}$			
Cl^-			
Ca^{+2}			
Mg^{+2}			
Na^+			

Addendum to June progress report

During this quarter, we have began to extend our model to account for the precipitation/dissolution of authigenic barite. Records of authigenic barite distribution in the sediments can be used to infer the depth of SMTZ, which can be linked to the strength of methane flux in the past. The complexity we are trying to address is that barite could be both authigenic and detrital origin. In our current kinetic model, the detrital input of barite could be accounted for by assigning boundary condition of barite; that can be time dependent. Moreover, the effect from organic matter degradation can be teased out by matching the observed TOC profile. Methane produced through methanogenesis can shallow the SMTZ. However, as our primary model results suggest, this amount of methane is not enough to account for the observed barite records. An external source of methane is required (i.e., methane inflow from outside the model regime). Our model is similar to the model developed by Arndt et al. (2006; 2009), which was applied to account for the authigenic barite records across the organic matter rich Cretaceous shale drilled on the Demara Rise. We are currently testing different combinations of external methane fluxes so that we can obtain the most possible combination. The following checklist summarizes our progress in this quarter:

Task	Subtasks	Status
TASK 2. Paleo-methane proxies (barite)	2.1 Set up the model framework: discretization of spatial and temporal modeling domain, setup of species (primary, secondary, gas, and minerals) considered, and thermodynamic and kinetic database entries.	done
	2.2 Integrate present day SMTZ model (Task 1) into this framework.	done
	2.3 Verify and adjust our model parameters with field observations.	ongoing
	2.4 Compare the results from CrunchFlow with our previous model	ongoing

References

Arndt S, Brumsack H-Jg & Wirtz KW (2006) Cretaceous black shales as active bioreactors: A biogeochemical model for the deep biosphere encountered during ODP Leg 207 (Demerara Rise). Geochim. Cosmochim. Acta 70: 408-425

Arndt S, Hetzel A & Brumsack HJ (2009) Evolution of organic matter degradation in Cretaceous black shales inferred from authigenic barite: A reaction-transport model. Geochim. Cosmochim. Acta 73: 2000-2022

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