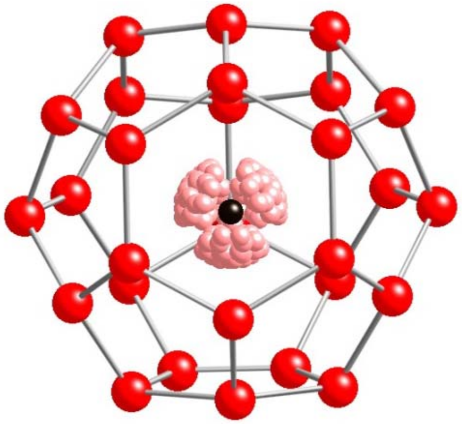
Methane hydrates
A source for slow methane release on Mars?

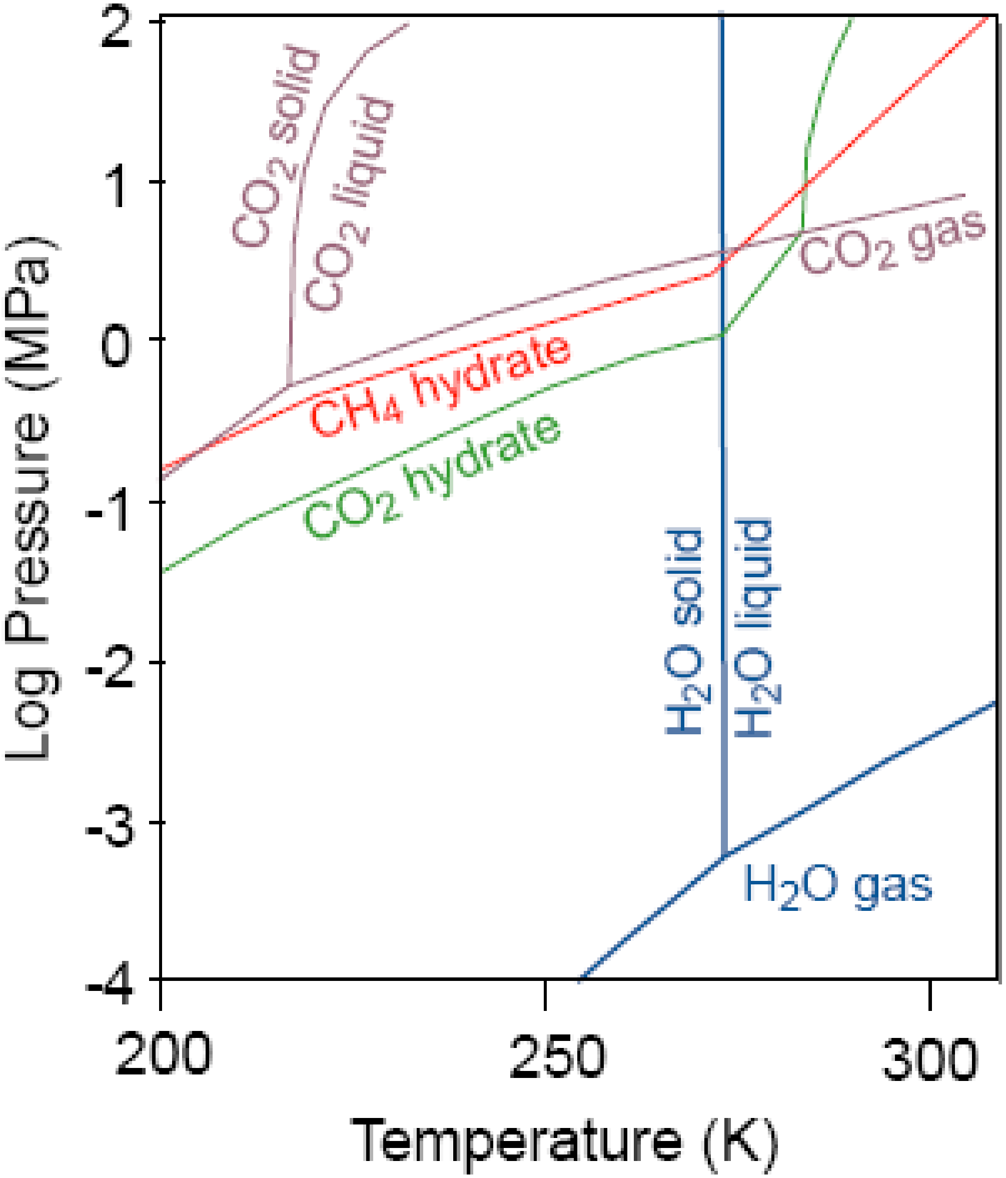
Megan Elwood Madden,
John Leeman, Brandon Guttery
School of Geology and Geophysics, University of Oklahoma
David Blackburn
Arkansas Center for Space and Planetary Science, University of Arkansas

SCHOOL OF GEOLOGY & GEOPHYSICS
The University of Oklahoma



Methane Hydrate:
$CH_4 * 5.75\ H_2O$

Rawn et al. in prep



Questions:

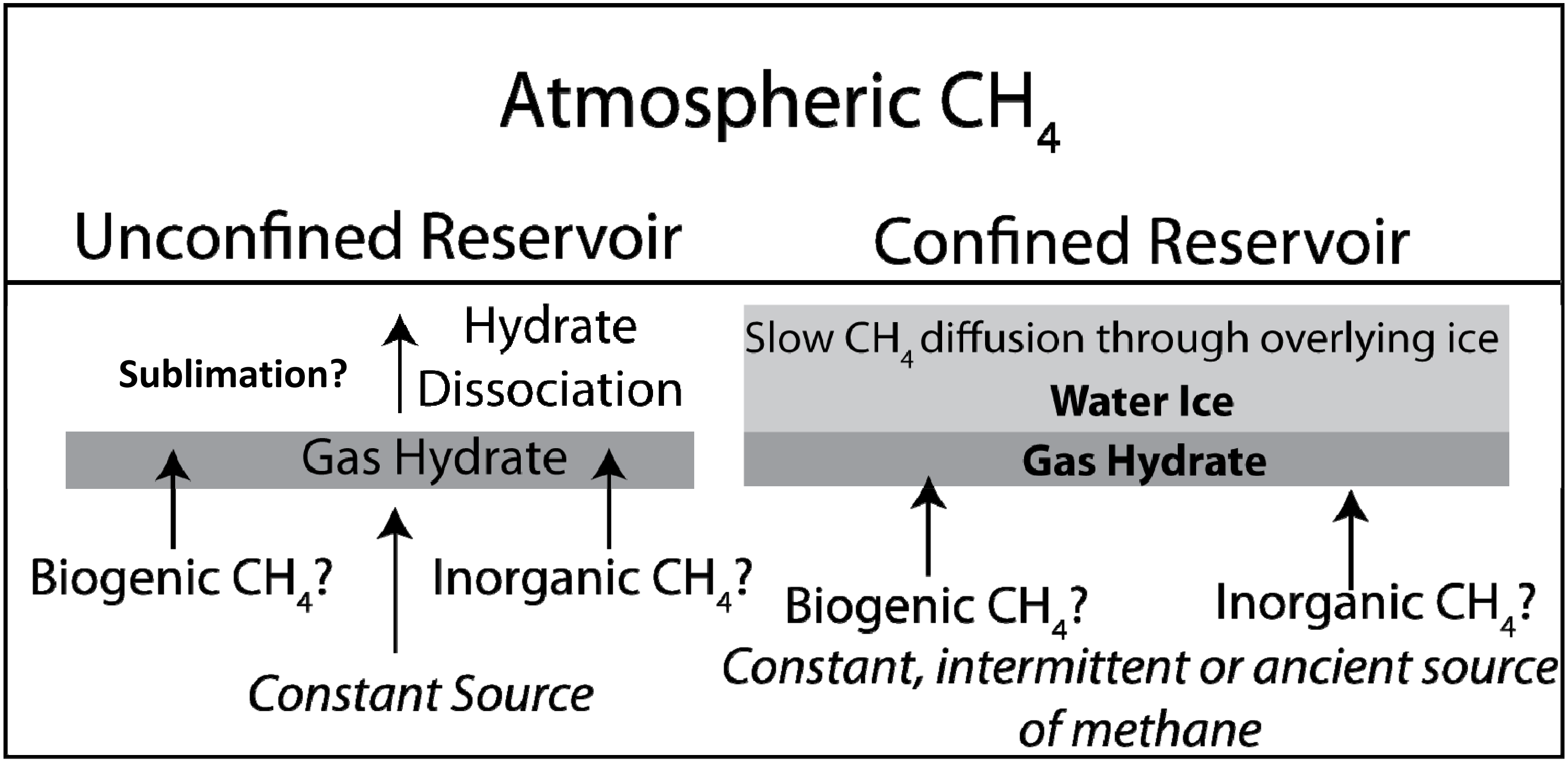
- What are the potential mechanisms for hydrate dissociation in the shallow subsurface?

- What are the local effects of hydrate dissociation? Are there feedbacks that need to be considered?

- What is the rate of hydrate dissociation?

- Could hydrate dissociation/formation provide fluxes of methane comparable to those observed on Mars?

Potential Gas Hydrate Reservoirs on Mars



Atmospheric CH_4

Unconfined Reservoir

Sublimation?

Hydrate Dissociation

Gas Hydrate

Biogenic CH_4?

Inorganic CH_4?

Constant Source

Confined Reservoir

Slow CH_4 diffusion through overlying ice

Water Ice

Gas Hydrate

Biogenic CH_4?

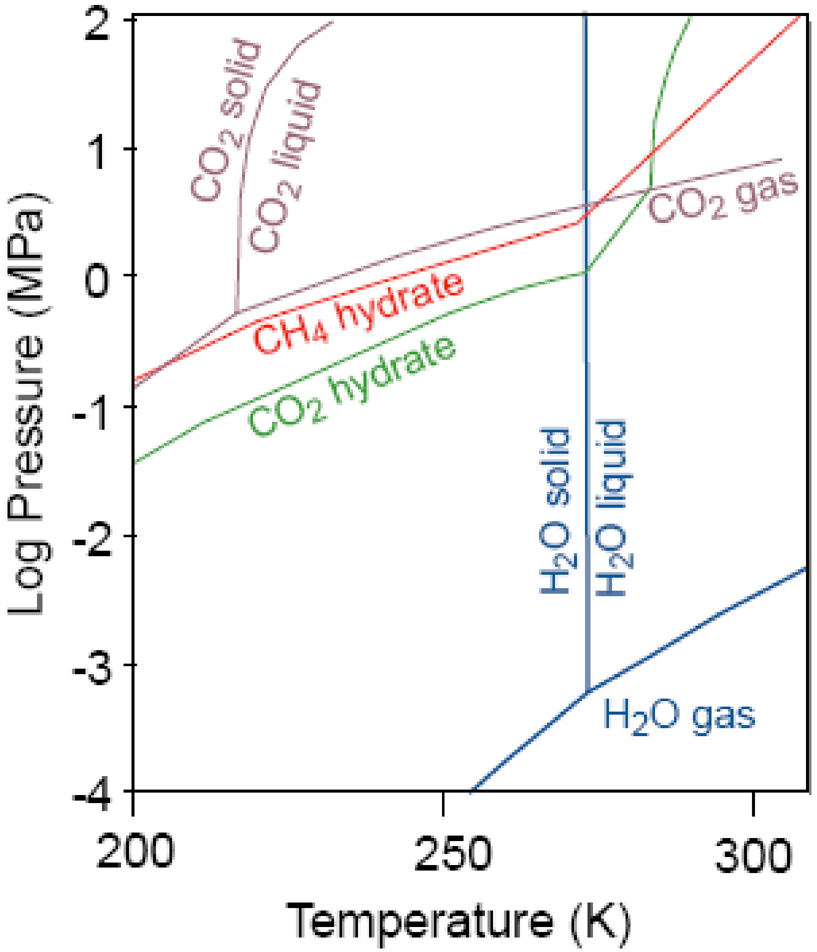
Inorganic CH_4?

Constant, intermittent or ancient source of methane

Hydrate dissociation mechanisms:

1. Increase Temperature
2. Decrease Pressure
3. Decrease Gas Concentration
4. Increase Salinity

All result in negative feedbacks

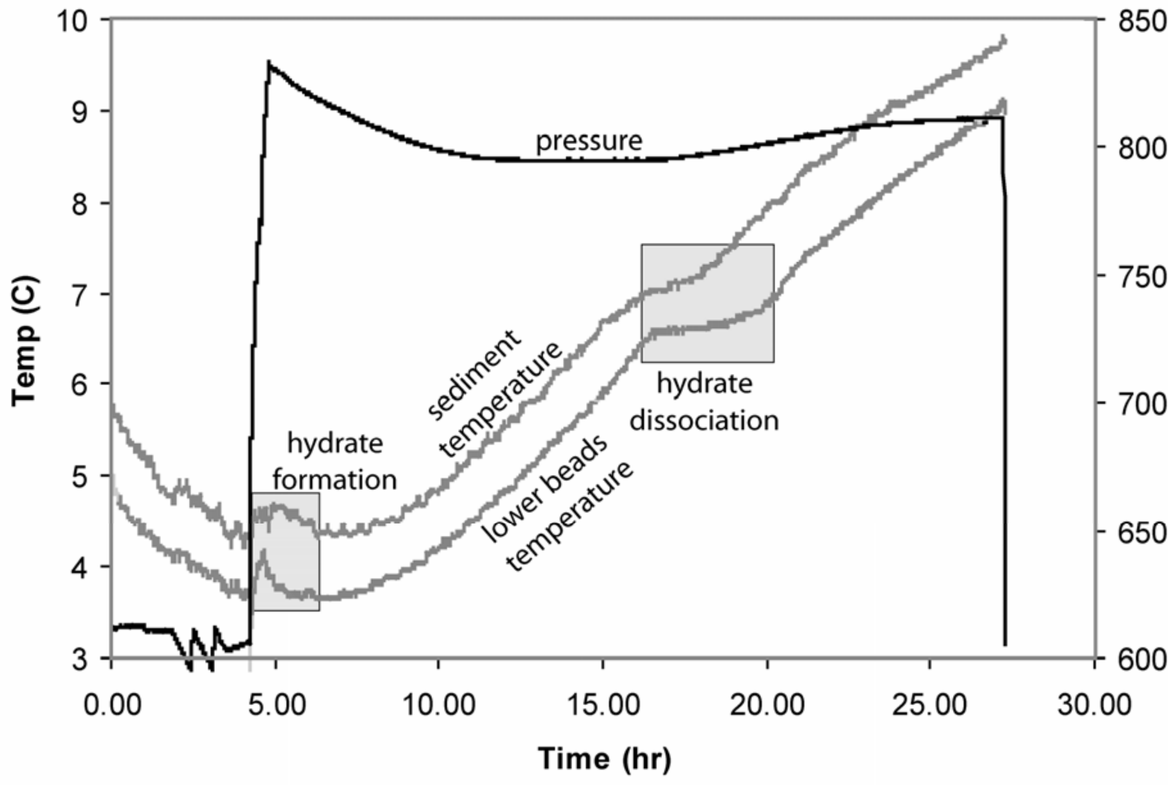


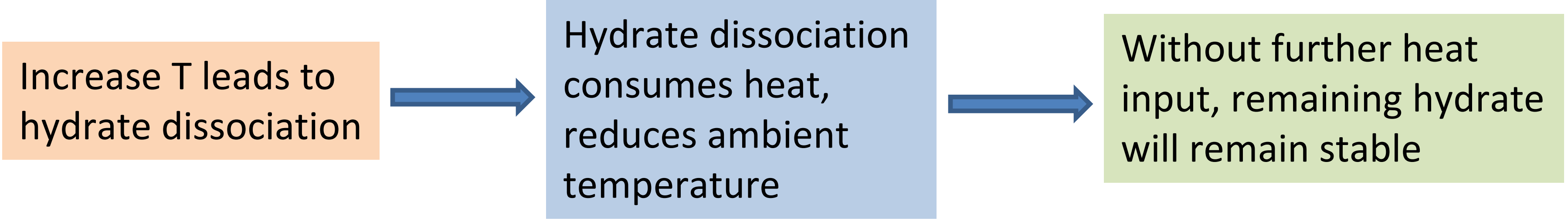
Increase in Temperature

Hydrate dissociation is an **endothermic** process

Temperature buffers

Constant heat source necessary for continuous dissociation





Increase T leads to hydrate dissociation

Hydrate dissociation consumes heat, reduces ambient temperature

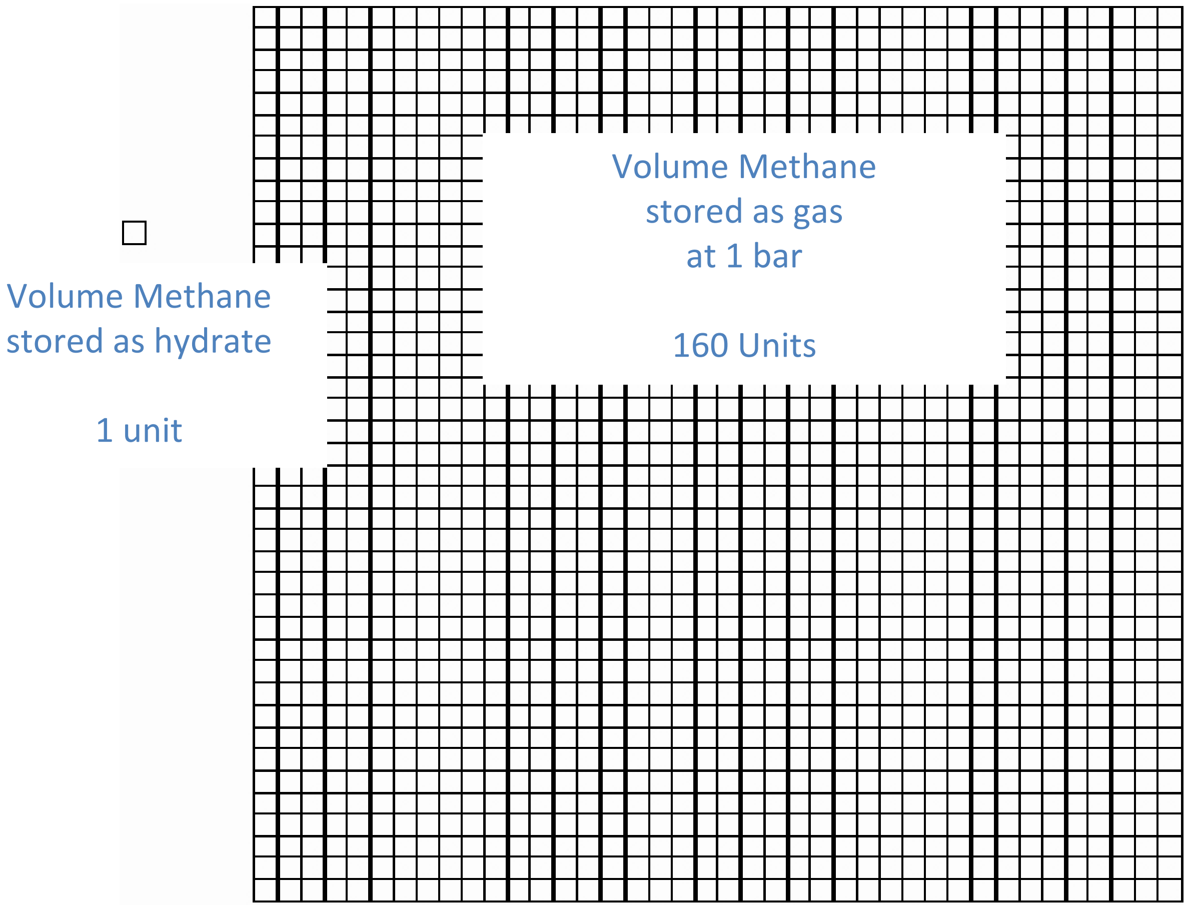
Without further heat input, remaining hydrate will remain stable

Decrease in pressure or gas concentration

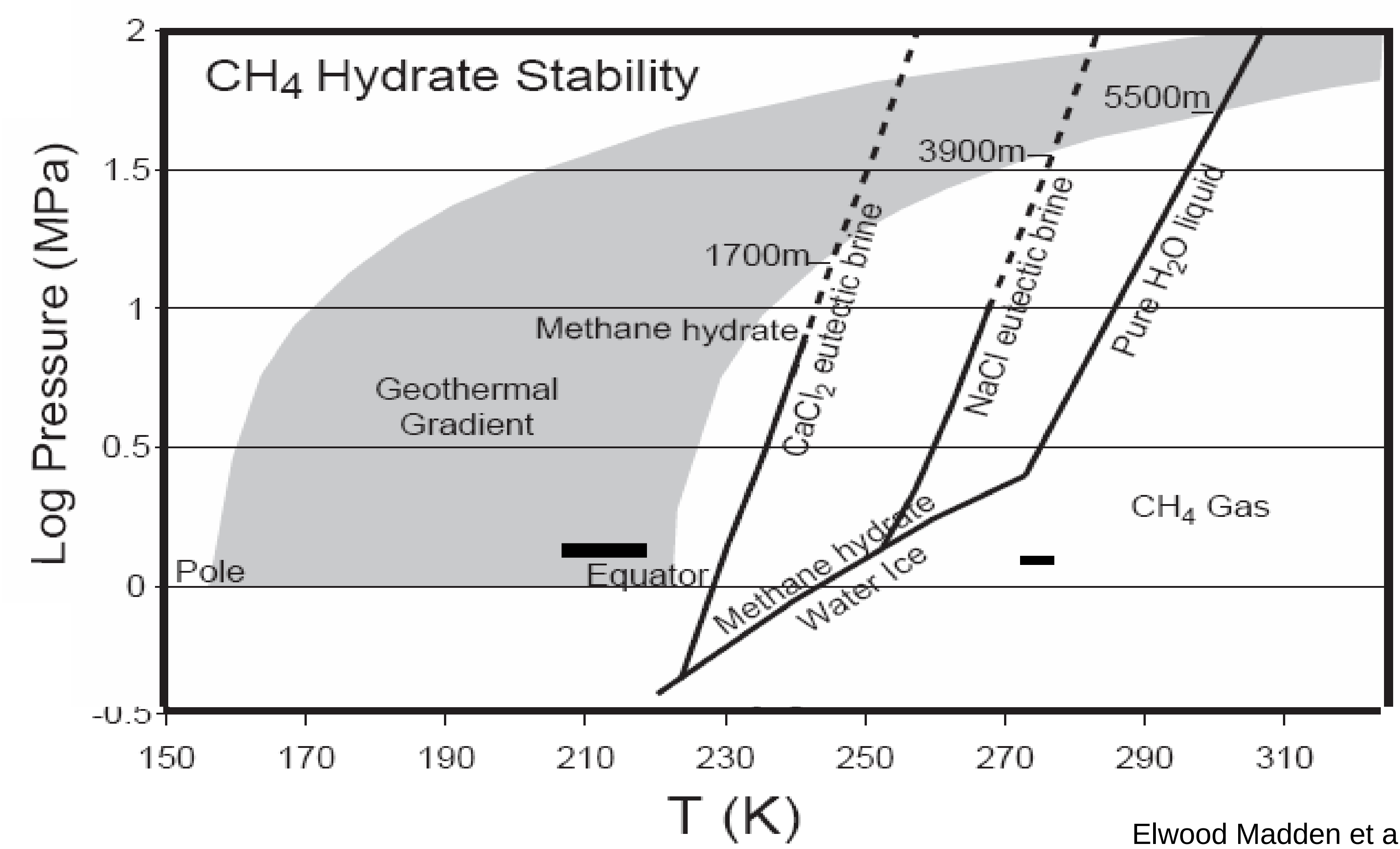
Decrease in P or X leads to hydrate dissociation →

160 Equivalent units of gas released →

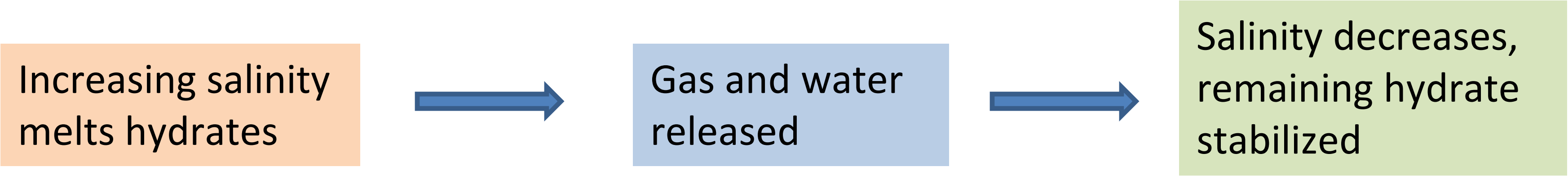
Pressure and gas concentration increase in a closed or semi-closed system, remaining hydrate stabilized



Salinity-induced hydrate dissociation



Elwood Madden et al. (2007 GRL)

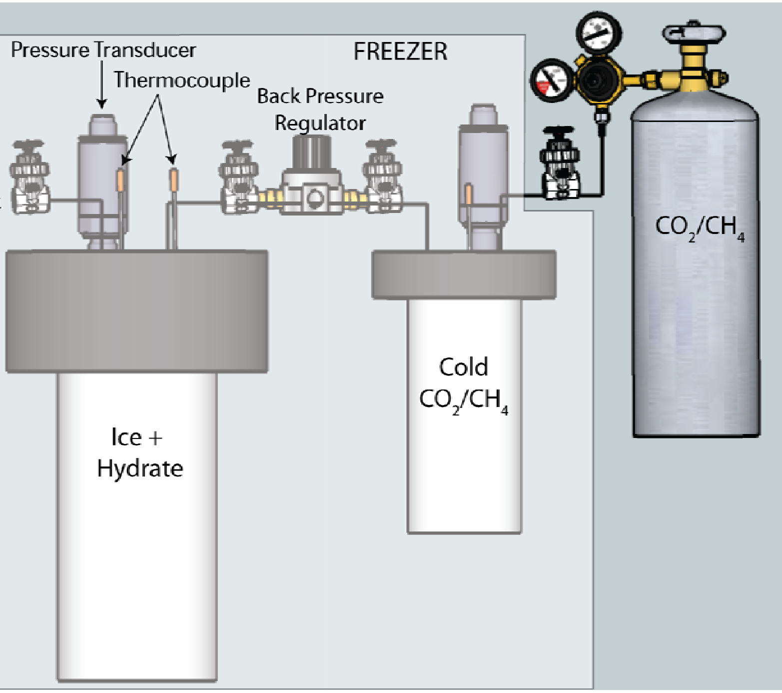


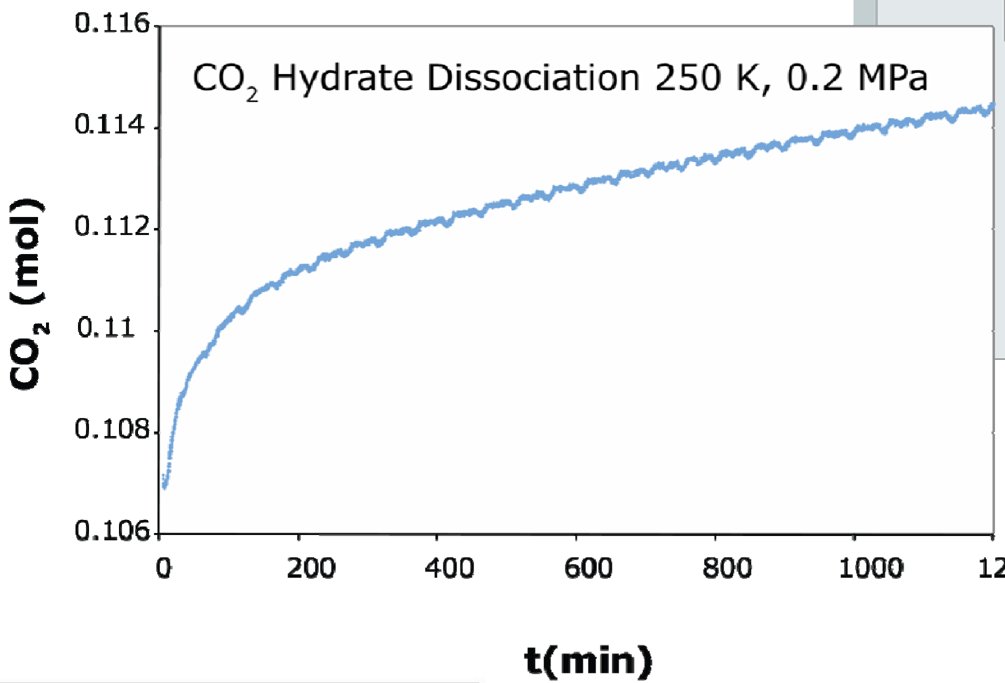
Increasing salinity melts hydrates

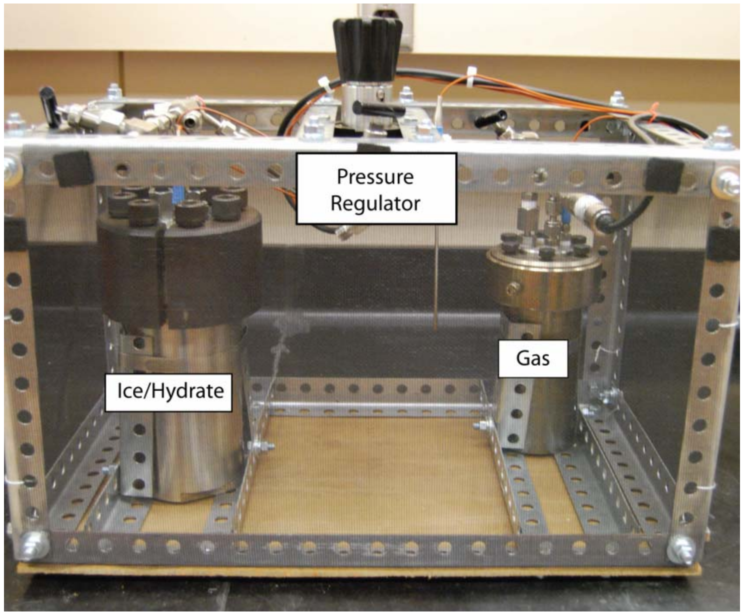
Gas and water released

Salinity decreases, remaining hydrate stabilized

Experimental Hydrate Dissociation Rates







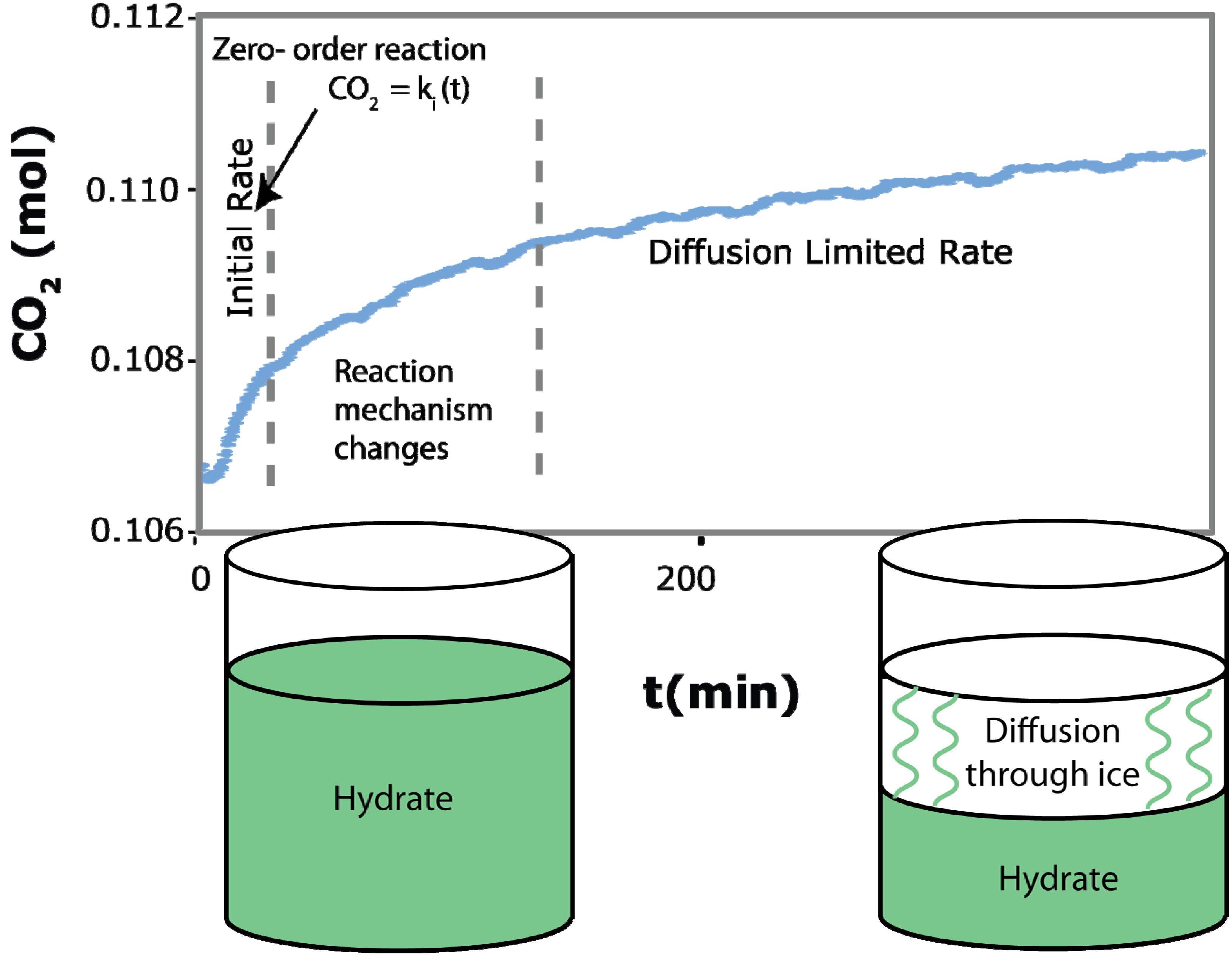
DANGER METHANE

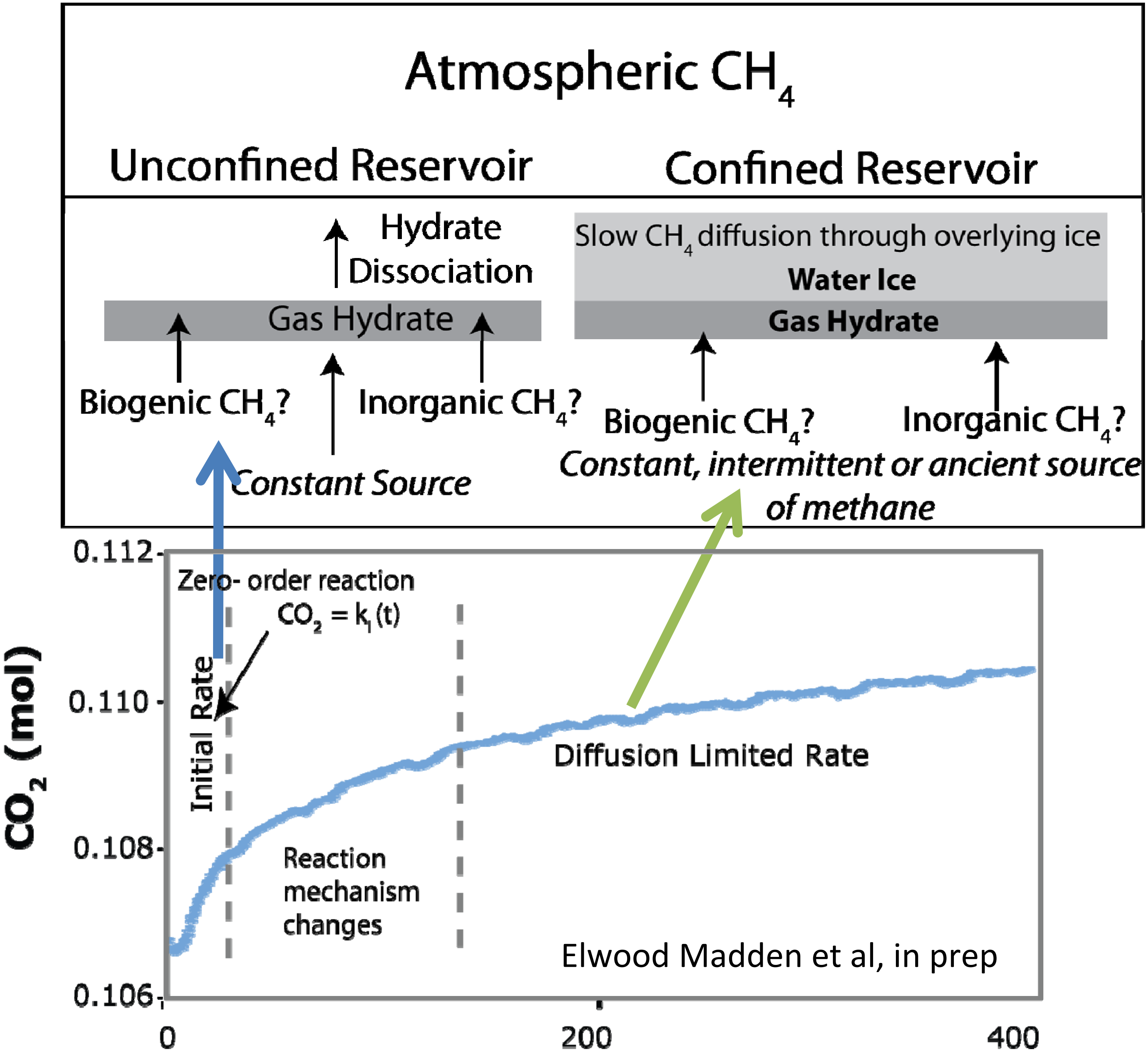
HIGHLY FLAMMABLE

- NO SMOKING
- NO MATCHES
- NO OPEN FLAMES

DO NOT ENTER IF ALARM IS SOUNDING
CONTACT M. ELWOOD MADDEN 405-325-1563 / 405-618-6275
OU POLICE 405-325-2864

Reaction Mechanism





Atmospheric CH_4

Unconfined Reservoir

Hydrate Dissociation

Gas Hydrate

Biogenic CH_4?

Inorganic CH_4?

Constant Source

Confined Reservoir

Slow CH_4 diffusion through overlying ice

Water Ice

Gas Hydrate

Biogenic CH_4?

Inorganic CH_4?

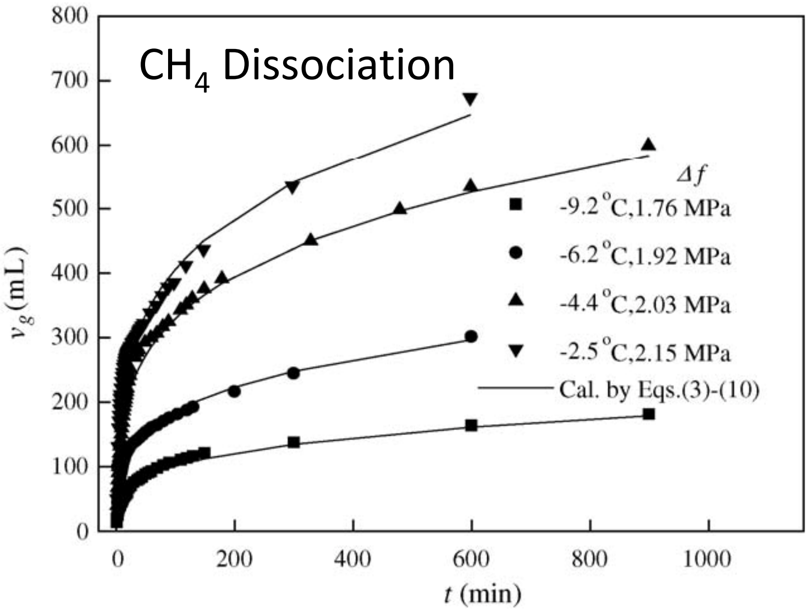
Constant, intermittent or ancient source of methane

Elwood Madden et al, in prep

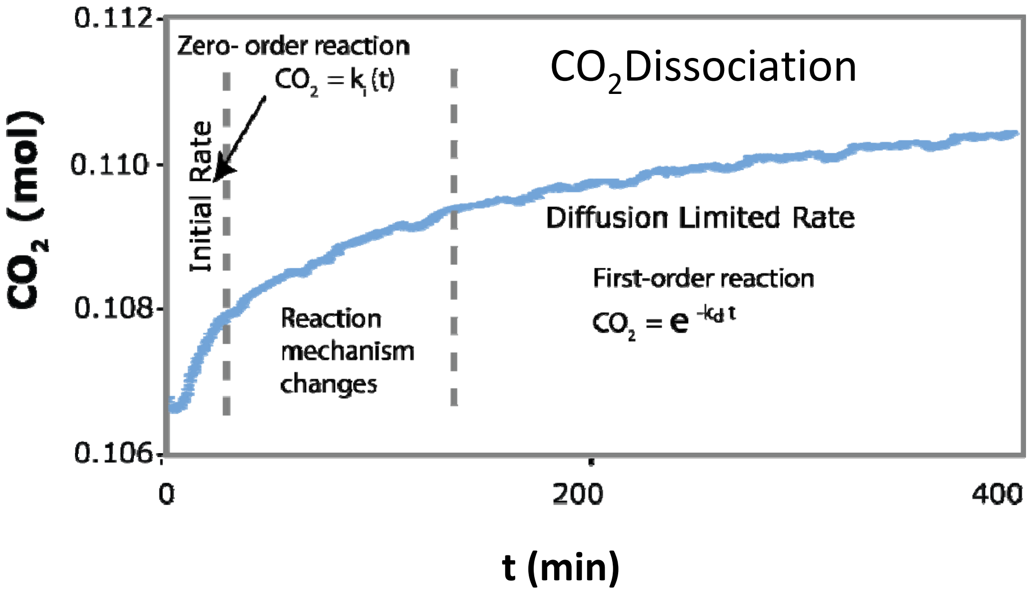
Rates of Hydrate Dissociation

Phases	P (Mpa)	T (K)	Rate/Diffusion Coefficient	Reference
CO_2 hydrate sublimation	3x 10^{-4}	250	3x 10^{-3} (mol/m^2s)	Blackburn et al., 2009
CO_2 hydrate → ice	0.2	250	7.9 x 10^{-4} mol/m^2s	*Initial Rate*
	0.2	250	2.1 x 10^{-5} mol/m^2s	*Diffusion-limited*
	0.1-0.3	270-273	4x 10^{-5} - 9x 10^{-5} (mol/s)*	Giavarini et al., 2007
CH_4 hydrate → ice	0.1-0.5	268-272	3 x10^{-14} – 2 x 10^{-13} m^2/s	Komai et al., 2004 (higher initial rates)
	0.1	264-270	1x 10^{-5} - 3x 10^{-6} (mol/s)*	Sun and Chen, 2006

* No surface area reported



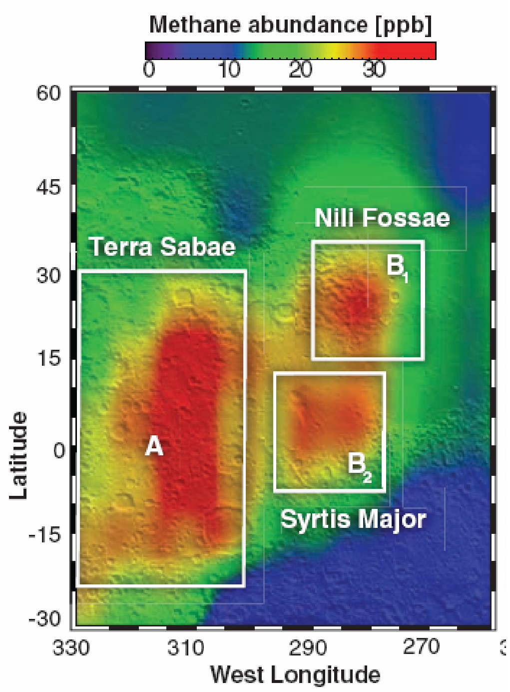
Sun and Chen, 2006



Elwood Madden et al, in prep

Hydrate source for seasonal methane plumes?

Constraints	**Rate (250 K)**	**Lateral area of reservoir (km^2)**
Observed plume	**1×10^{-11} mol/m²/s**	9.7×10^6
Terrestrial tundra	**1×10^{-9} mol/m²/s**	6000 (120 days)
Unconfined Hydrate Reservoir-dissociation	**8×10^{-4} mol/m²/s**	0.143 (120 days)
Unconfined Hydrate Reservoir-sublimation	**3×10^{-3} mol/m²/s**	0.04 (120 days)
Confined Hydrate Reservoir	**2×10^{-5} mol/m²/s**	5.4 (120 days) *or* diffusion through 40 m of ice



Mumma et al. 2009

Relatively small hydrate reservoirs could produce the observed plumes.

Formation of methane hydrates as a surface sink?

Phases	**P (Mpa)**	**T (K)**	**Rate/Diffusion Coefficient**	**Reference**
CO_2 hydrate sublimation	$3x\ 10^{-4}$	250	$3x\ 10^{-3}$ (mol/m^{2}s)	Blackburn et al., 2009
CO_2 hydrate → ice	0.3	250	$8\ x\ 10^{-4}$ mol/m^{2}s	*Initial Rate*
	0.3	250	$2\ x\ 10^{-5}$ mol/m^{2}s	*Diffusion-limited*
	0.1-0.3	270-273	$4x\ 10^{-5}$ - $9x\ 10^{-5}$ (mol/s)*	Giavarini et al., 2007
CH_4 hydrate → ice	0.1-0.5	268-272	$3\ x10^{-14}$ – $2\ x\ 10^{-13}$ m^2/s	Komai et al., 2004 (higher initial rates)
	0.1	264-270	$1x\ 10^{-5}$ - $3x\ 10^{-6}$ (mol/s)*	Sun and Chen, 2006
Ice → CO_2 Hydrate	0.7	250	$2\ x\ 10^{-4}$ mol/m^{2}s	*Initial Rate*
Ice → CO_2 Hydrate	0.7	250	$3\ x\ 10^{-5}$ mol/m^{2}s	*Diffusion-limited*
Ice → CH_4 Hydrate	1-2	245-270	$2\ x\ 10^{-6}$ - $2\ x\ 10^{-4}$ mol/m^2/s	Initial Rate, KUHS et al., 2006
Ice → CH_4 Hydrate	1-2	245-270	$2\ x\ 10^{-14}$ m^2/s	Diffusion limited, KUHS et al., 2006

At 150K, $5.3\ x\ 10^{-3}$ MPa (53 millibars) P(CH_4) needed to form hydrate

Conclusions

- All mechanisms result in a negative feedback for hydrate dissociation at local scales.
- Sublimation rate > Open system dissociation > Diffusion-limited dissociation
- Rates of dissociation are more than sufficient to produce observed methane concentrations, even considering the negative feedbacks.
- Rates of formation exceed methane uptake rate needed to explain plumes, but mechanism required to re-concentrate methane.

Future Work

- Determine rates of CH_4 hydrate dissociation and compare to CO_2
- Determine rates at low T, determine activation energy
- Determine effect of pressure

Acknowledgements: Andrew Madden, Seth Gainey, Margaret Root, Robert Turner

Funding: ORAU Powe Award, NASA Planetary Geology and Geophysics, OU VP Research