

marine
How gas hydrates form in Nature

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Rice U. Hydrate Workshop

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HYDRATE FORMATION CONDITIONS

- gas hydrate forms in methane-saturated formation waters under conditions of high P and low T
- stability conditions widespread (>70% of earth's surface), but methane content limits occurrence
- methane present in marine sediments only where accumulate rates $> 40\text{-}50 \text{ m ma}^{-1}$ (otherwise sulfate not depleted and methane not generated or oxidized)

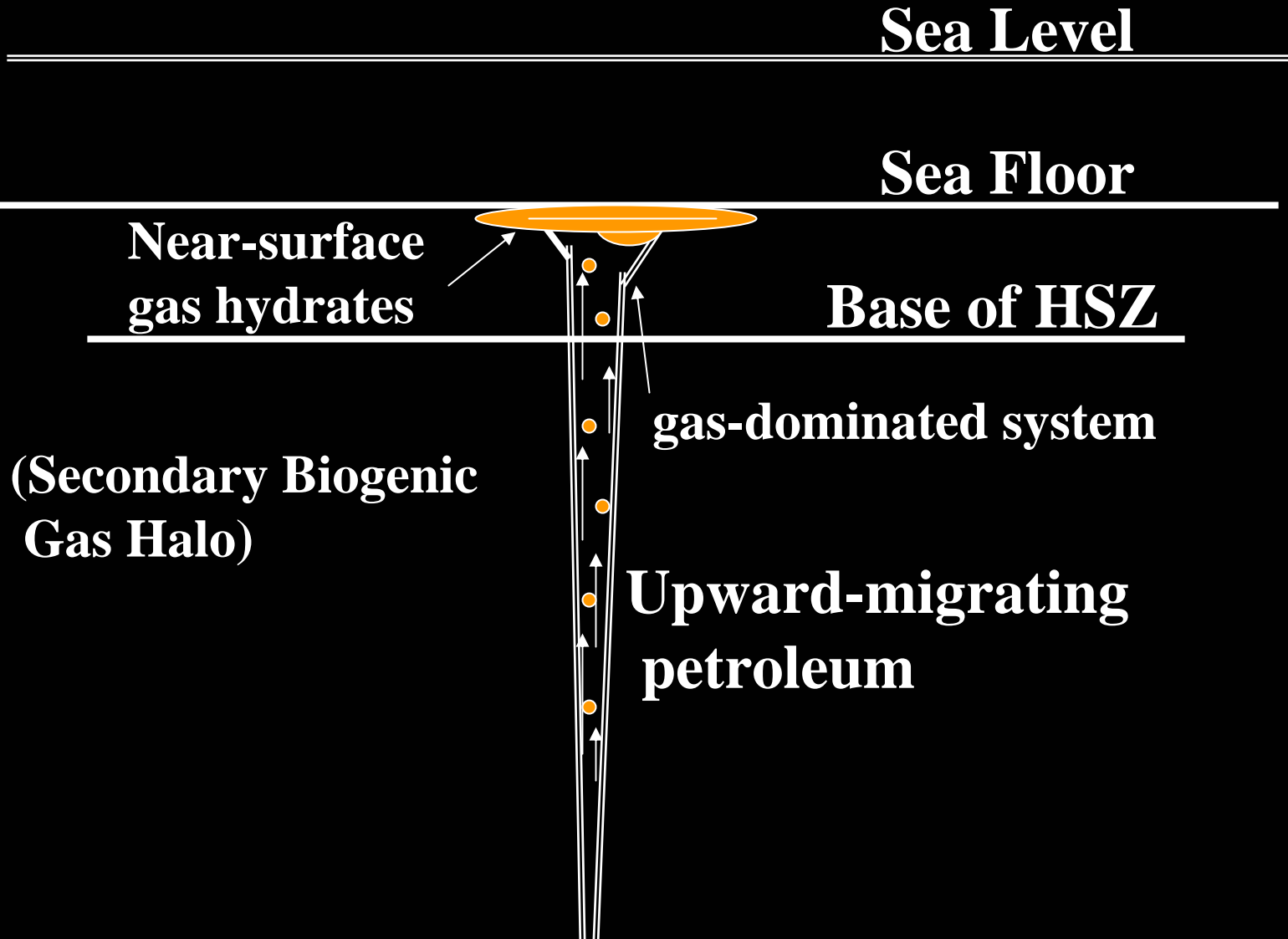
Outline: Main points

1. Modes of marine gas hydrate occurrence
2. Hydrates as a safety factor preventing overpressure
3. Evidence for and importance of shallow microbial processes for marine gas hydrate occurrence

MARINE GAS HYDRATE OCCURRENCE--2 MODES

- **Near-surface, thermogenic gas hydrates, gas-dominated system;**
- **BSR-related, biogenic gas hydrates, water-dominated system.**

Sea floor, thermogenic gas hydrates



Biogenic (BSR-related) gas hydrates

Sea Level

Sea Floor

Top HSZ

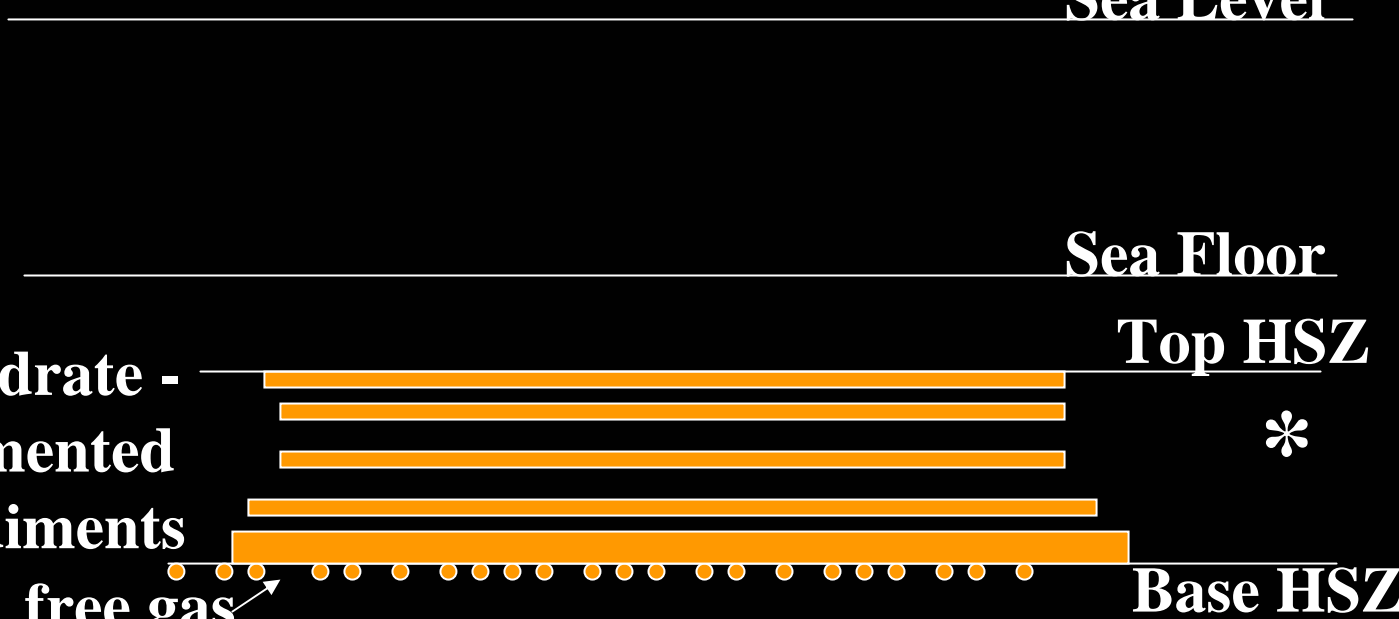
Hydrate -
cemented
sediments

free gas
(minor)

*

Base HSZ

* internally-generated gas,
water-dominated system

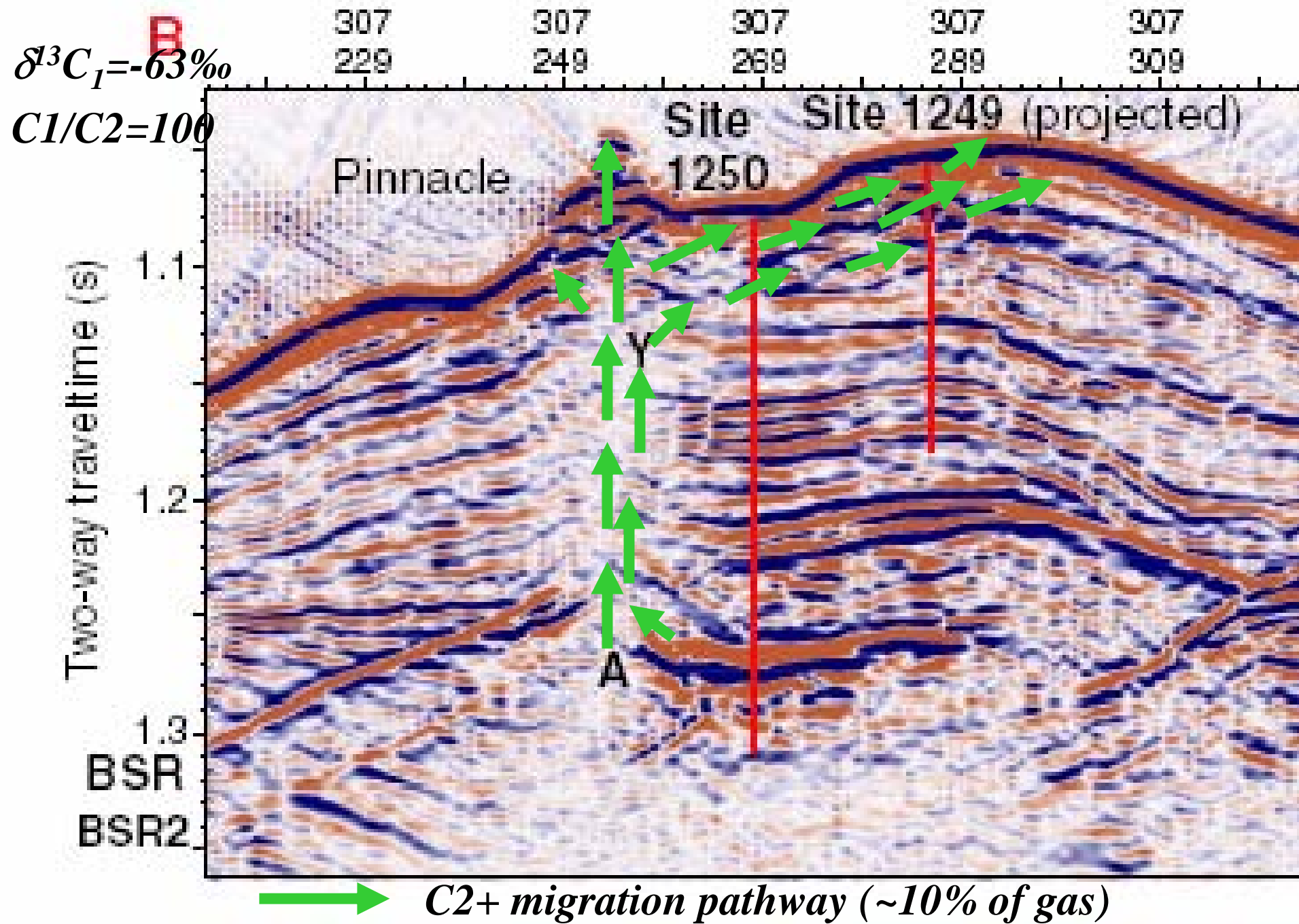


MARINE GAS HYDRATE OCCURRENCE--2 MODES

- *transport dominated* hydrates, usually near-surface with thermogenic gas
- *reaction dominated* hydrates, microbial methane, usually with BSR

ODP Leg 204 Results

- Gas hydrates abundant (>20%) in shallow zones (0-40 mbsf) only at/near summit—*transport dominated*
- Away from summit, gas hydrates present at lower concentration (0-3%) in deeper zones (45-195 mbsf)—*reaction dominated*

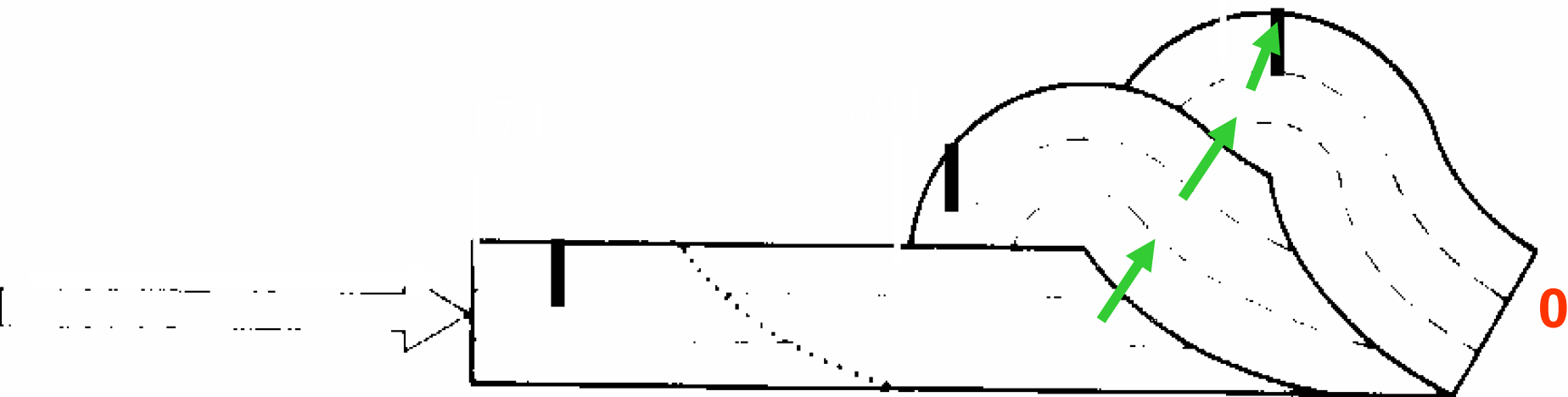
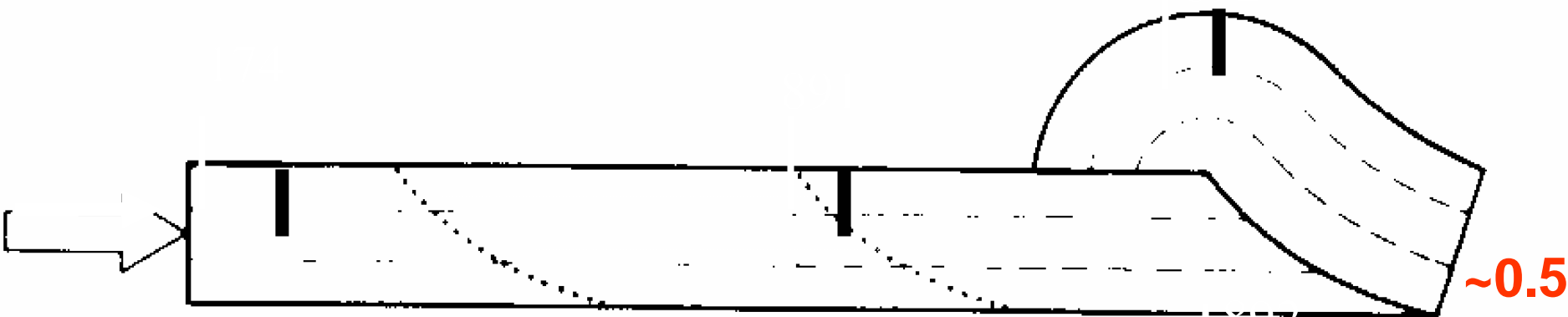
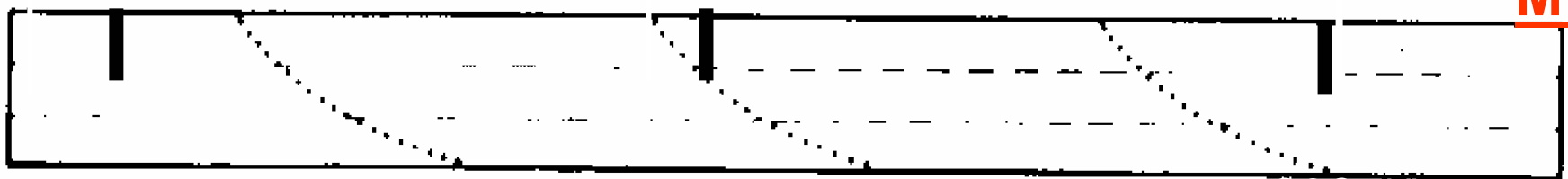


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891

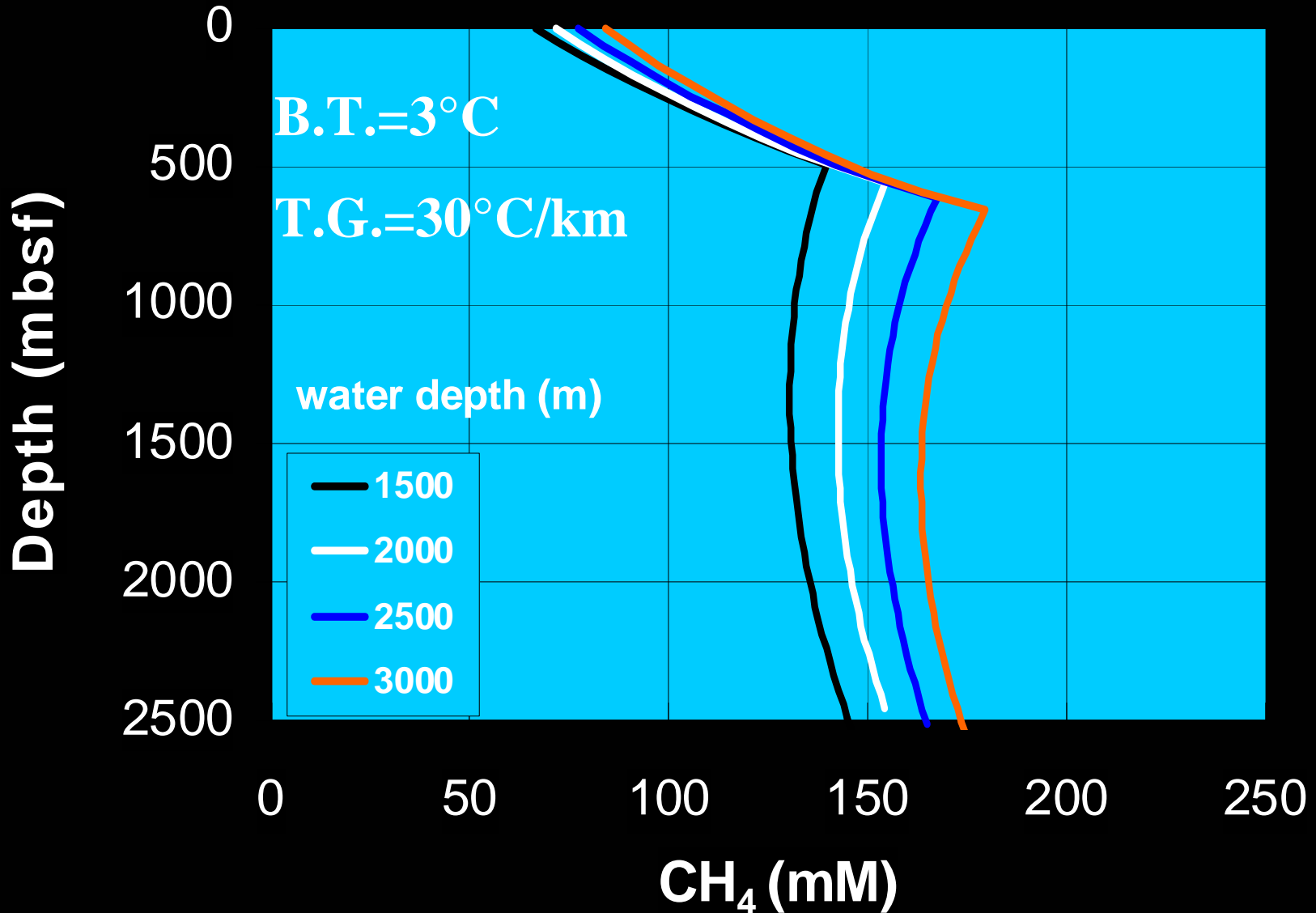
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MYBP



Imbricate Thrust Trench-Slope Model (Seely et al., 1974)

CH₄ solubility in porewater

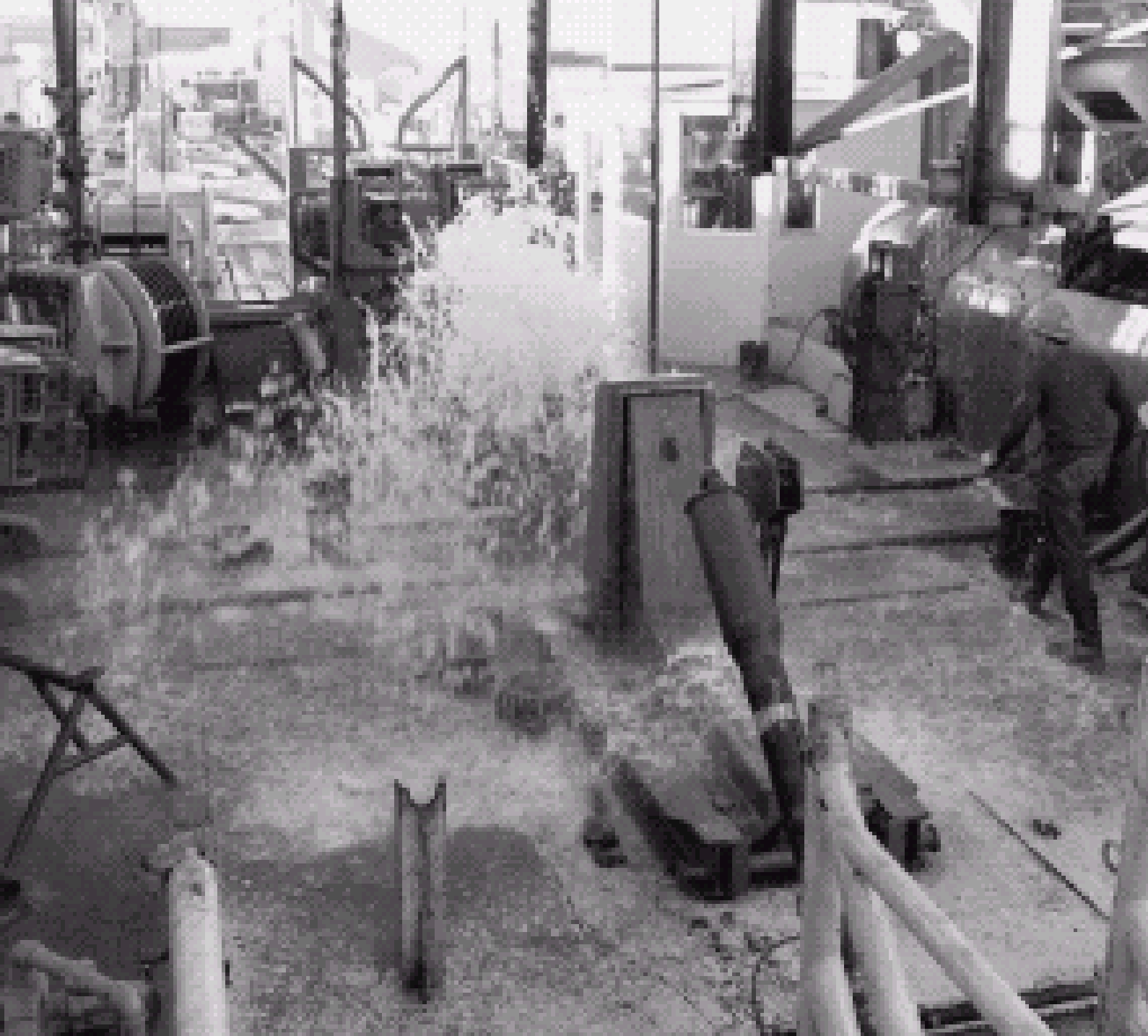


Accretionary prisms

- **Combine elements of both modes of hydrate occurrence**
- **Enhanced CH₄ transport due to more intense dewatering of sediments and fault/fracture conduits**
- **More CH₄ available for hydrate by pressure reduction associated with tectonic uplift**

DSDP/ODP EXPERIENCE

- Prior to Nov. 1991 no intended DSDP/ODP drilling beneath BSR due to presumed gas hazard
- Policy revised by expectation that hydrate equilibrium fixes gas pressure at hydrostatic
- No drilling/safety problems on ODP Legs where BSR/BHSZ penetration permitted (141, 146, 164, 170, 190, 196, 202, 204)



*Leg 174A
Fountain*

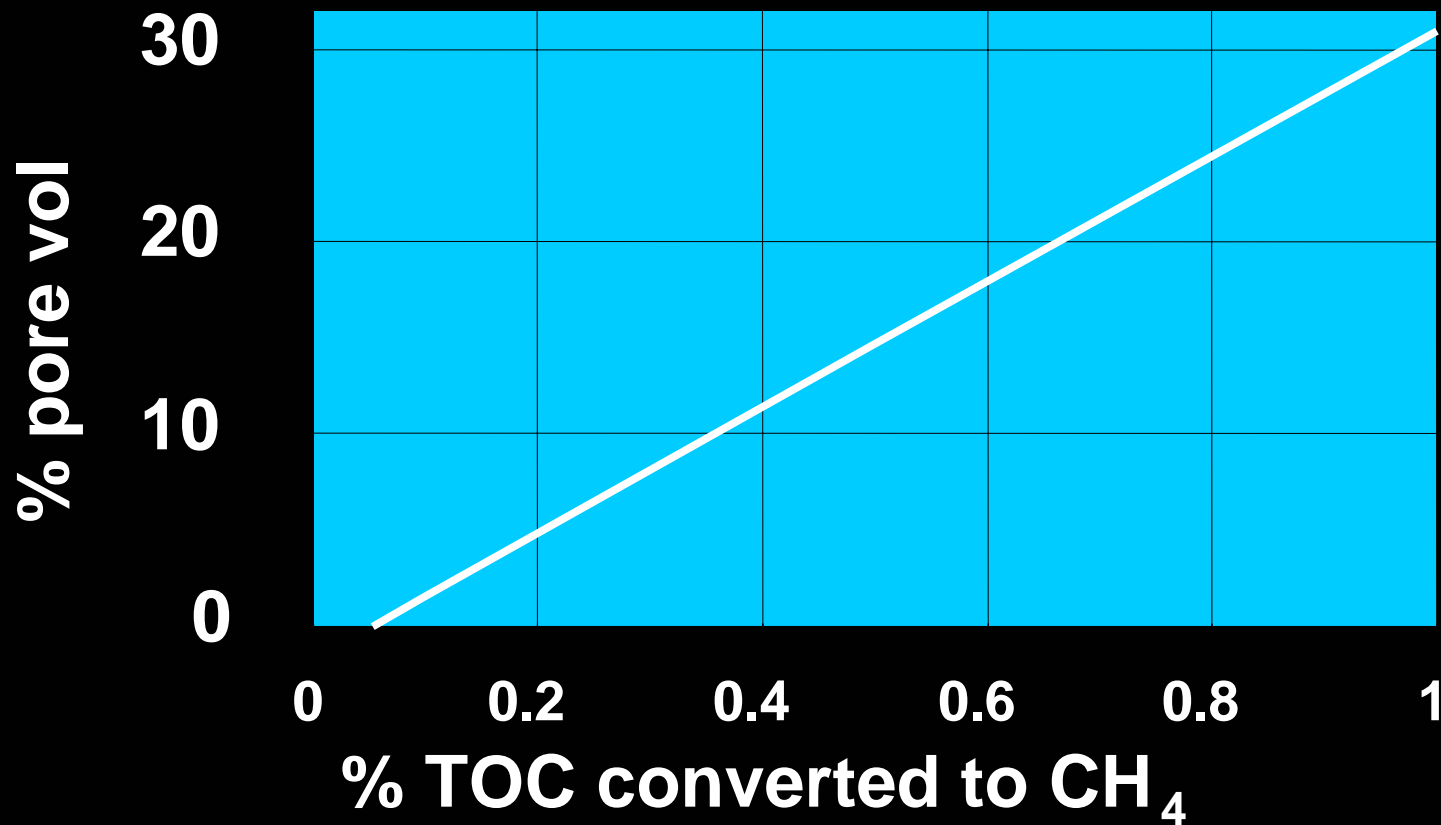
*Initially
30m high
gusher of
water-sand*

Equilibrium control on gas pressure and saturation

- **3-phases (gas-liquid-solid) required if hydrates present at base HSZ.**
- **Pressure fixed (hydrostatic) at base HSZ.**
- **Thick gas column unstable beneath gas hydrate--buoyancy causes reaction and removal of gas to form more hydrate.**
- **Gas beneath HSZ at residual saturation levels**

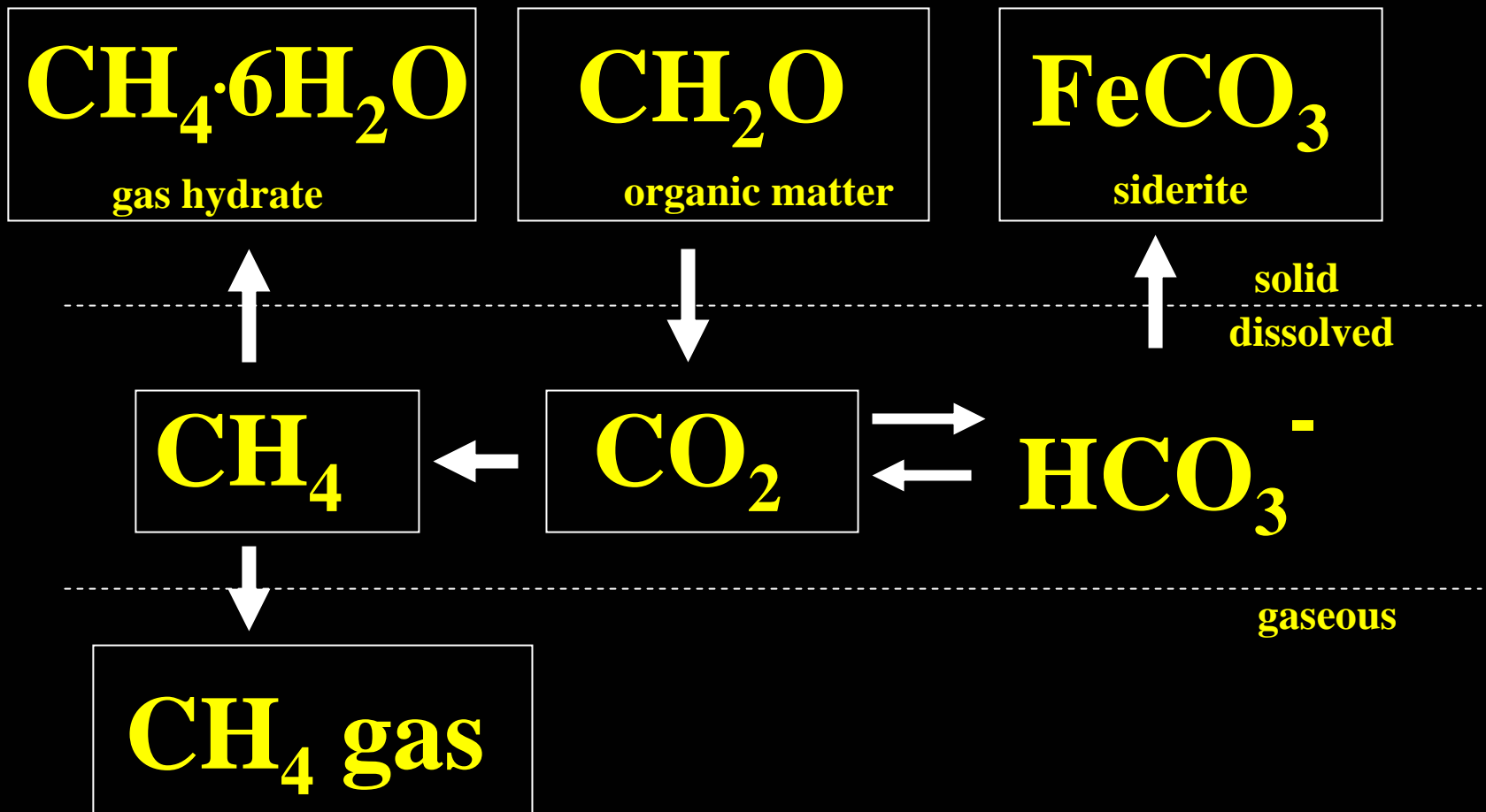
microbial CH₄ generation

- Remineralization of 0.1 wt% TOC gives 217 mM CH₄



*assuming 50% porosity, 2.6 g/cc grain density

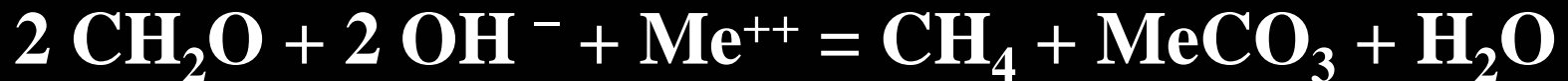
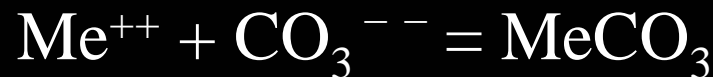
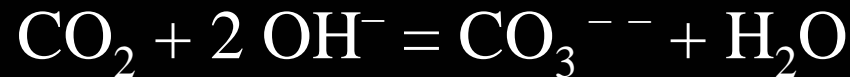
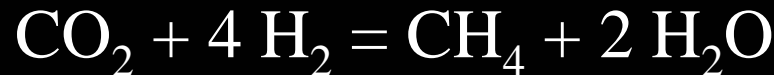
Carbon flow during Methanogenesis



Sediment phase partitioning

- Solids accumulate at favored sites controlled by surface tension/nucleation phenomena (pore size, capillary pressure, bioclastic nuclei)
- CH₄ supersaturation can be maintained in fine-grained sediments
- Burial of pore water and solids decoupled due to compaction

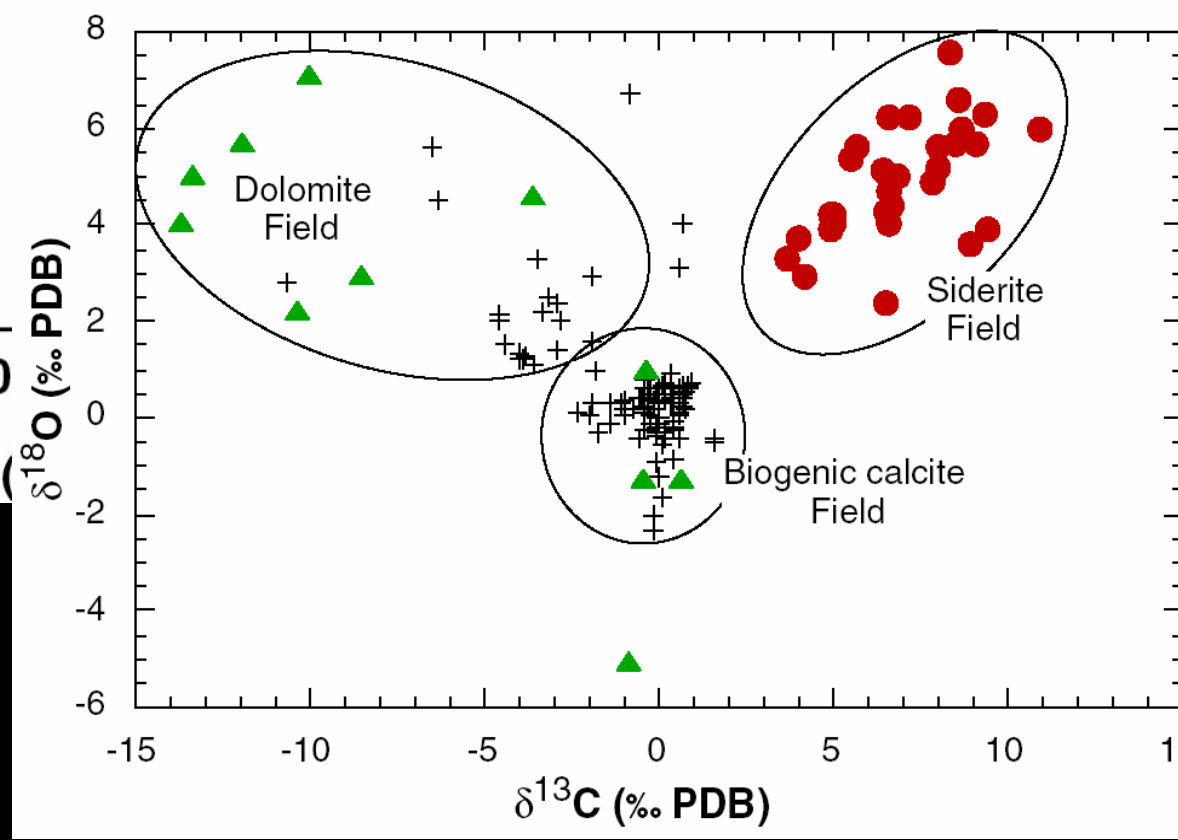
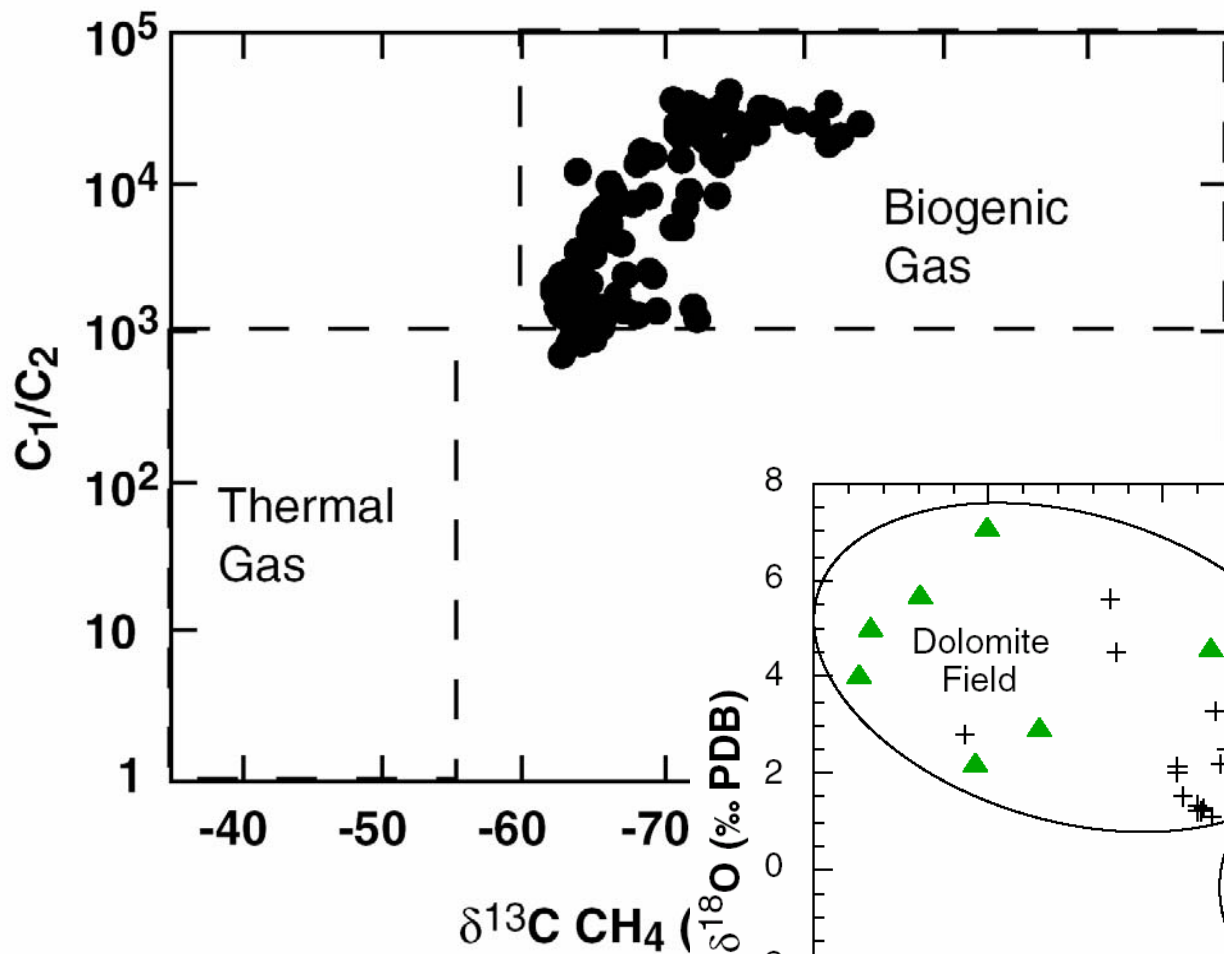
Carbon & isotopic mass balance for coupled CH₄ and MeCO₃ production



-22.5‰

-65‰

+20‰

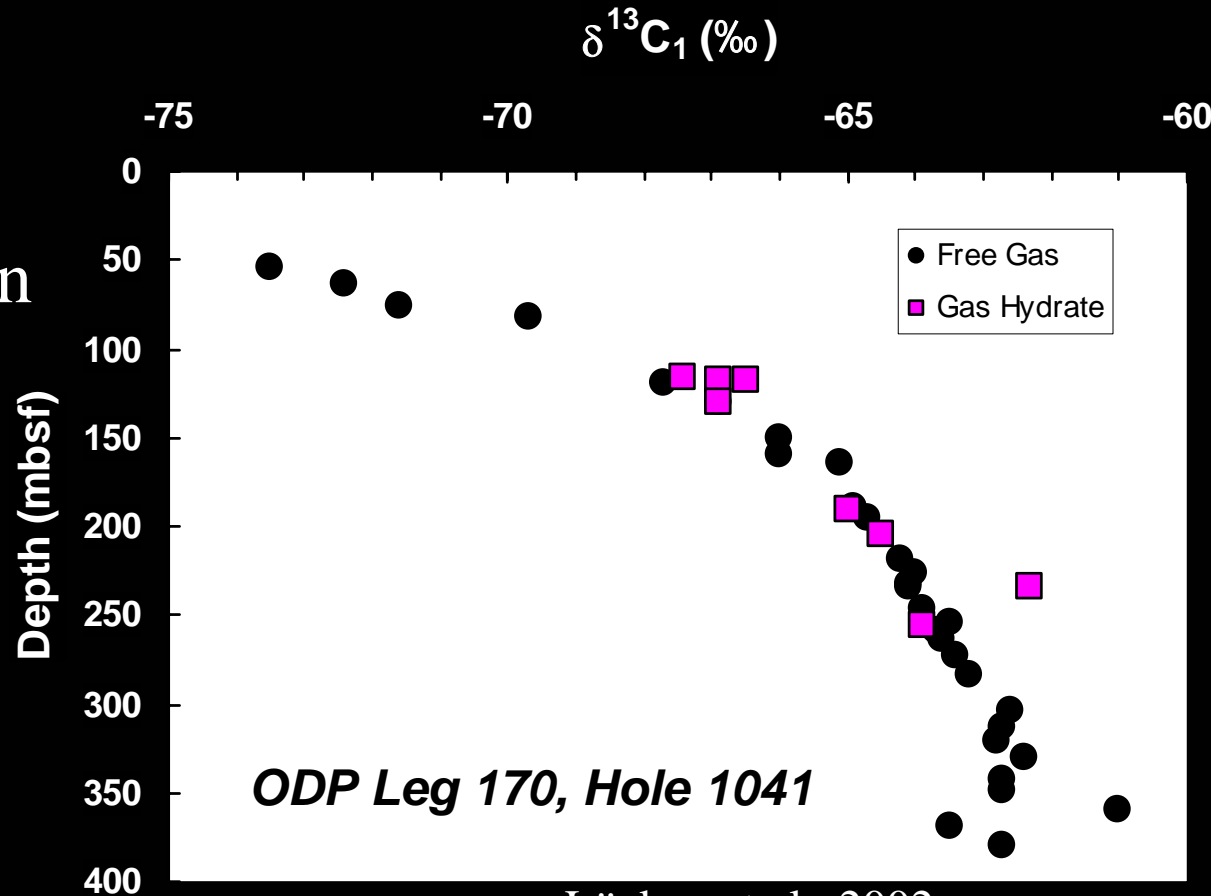


Paull et al., 2000 (164 SR)

Rodriguez et al., 2000 (164 SR)

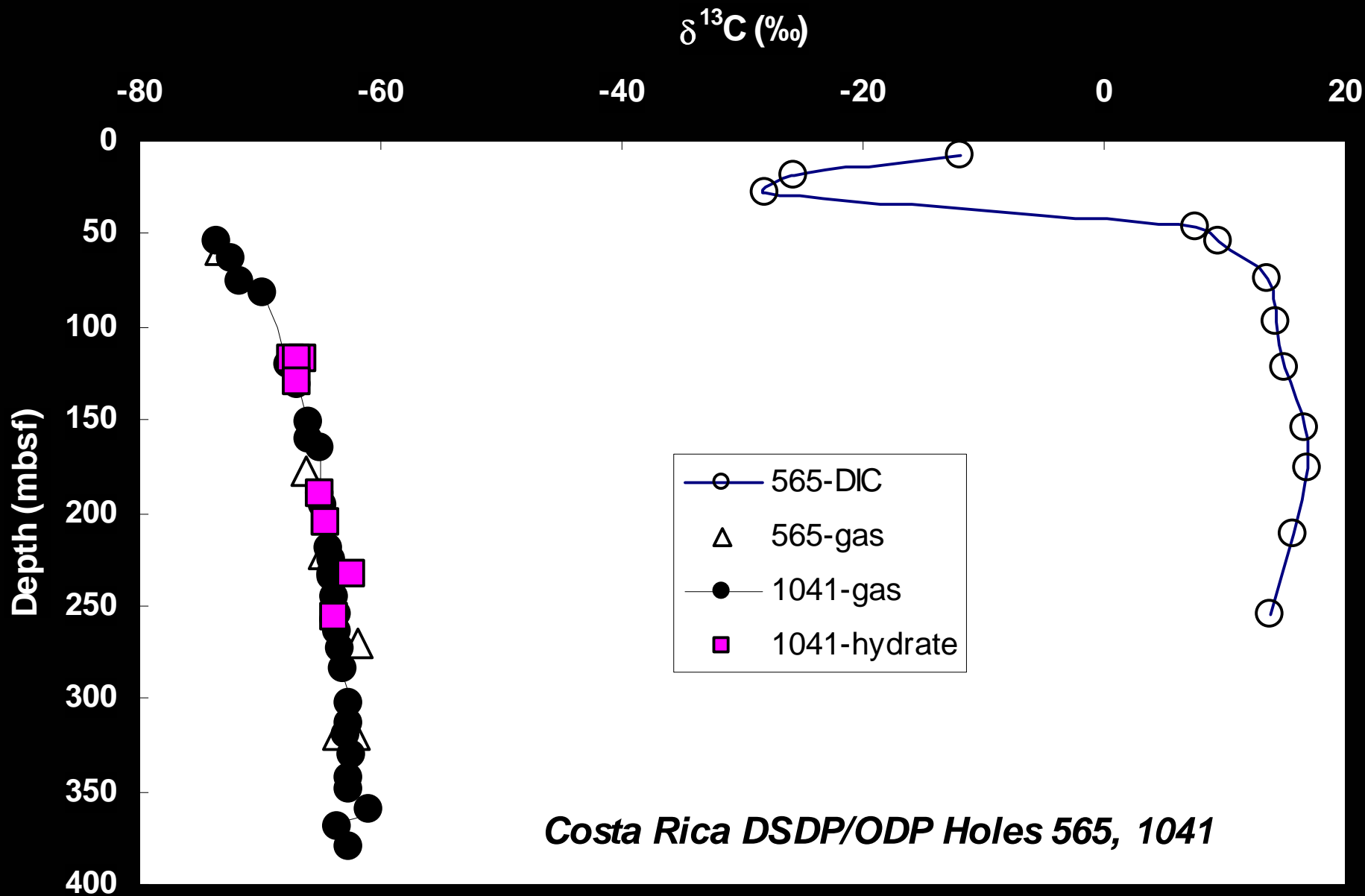
Locally generated hydrates have variable $\delta^{13}\text{C}_1$, but same as gas from adjacent cores

- Reaction gradient from ^{12}C -depletion in substrate CO_2
- Transported gas unrelated to shallow microbial process



Lückge et al., 2002

M. Kastner, pers. commun.



Conclusions--I

- CH_4 is limiting factor for gas hydrate formation (0.1% TOC converted to CH_4 at $\phi = 0.5$ yields 217 mM).
- Most microbial CH_4 generated at relatively shallow depths (50-500m), but can be buried and remobilized.
- Migrating thermogenic gas forms hydrates near sea floor, requires gas-dominated (dry) pathways through HSZ.

Conclusions--II

- Free gas required (by phase rule) if hydrate present at base of HSZ.
- Free gas limited to residual saturation levels (5-10%) at hydrostatic pressure in water-dominated system.
- Gas accumulations capped by marine gas hydrates in water-dominated systems probably subeconomic.